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DETERMINATION OF EFFECT OF PARTICULATE EXHAUST EMISSIONS OF ADDITIVES AND IMPURITIES IN GASOLINE

DOW CHEMICAL COMPANY

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Research was conducted to develop test methodology to determine the effect of fuel additives on particulate emissions from conventionally equipped (non-catalyst) automobiles. Utilizing techniques developed in previous research, scientists tested the effect of a manganese containing additive and a nitrogen containing additive for comparison with baseline runs. Repeatability and reproducibility of test conditions were determined for a wide variety of analytical techniques. The utility of these techniques was also investigated. In addition, a survey of future trends in fuel additive technology was made; results were inconclusive due to insufficient responses of those surveyed.

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FOREWARD

This report was prepared by the Transportation Chemicals Research Group, Ag-Organics Department, The Dow Chemical Company, Midland, Michigan, under Contract 68-02-0332. The work reported herein was administered under the direction of the Office of Air and Water Programs, Environmental Protection Agency, with John E. Sigsby, Jr., serving as Project Officer.

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The authors of this report are James E. Gentel, Otto J. Manary, and Joseph C. Valenta.

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ABSTRACT

This report describes work carried out to develop a methodology for the determination of the effect of fuel additives on exhaust particle size, concentration, and composition, from light-duty vehicles.

In order to determine the best methodology, particulate emissions were examined using a 350 CID Chevrolet engine, and several 350 CID Chevrolet vehicles. The engines and vehicles were operated under steady-state cruise conditions, and under the federal 23-minute cycle. Particulate mass measurement techniques have included tailpipe measurement methods and air dilution sampling methods using impaction separators, and filters.

Two different fuel additives as well as a baseline fuel were used to determine the validity of the methods employed. The engine dynamometer runs were correlated with vehicles using the same fuel and additives. Engine runs were made using both manufacturer's suggested and higher than suggested additive concentrations.

The data collected suggests that the methods employed do allow the determination of any adverse effects on particulate emissions due to the inclusion of an additive in the fuel. In addition, a study was made of probable trends in fuel additive chemistry.

An additional task of this study was the collection and analyses of exhaust gas condensate, to be used in animal health studies.

I. INTRODUCTION

The use of fuel additives has been shown to have an effect on the size, quantity, and composition of particulate matter emitted from light duty gasoline engines. Work involving particulate measurements primarily on leaded and unleaded fuel has been reported in EPA-R2-72-066. The purpose of the study covered in this report was to determine methodology for assessing the effect on particulate emissions of other types of fuel additives.

This study, performed from December 1971 to July 1973, is part of a fuel additive study program which was developed by EPA to determine the total range of fuel additive effects on emissions, and to develop methodology, where appropriate, to assist in the generation of data which is required by EPA for fuel additive registration. Other contracts in the fuel additive program include studies on the effect of fuel additives on the composition of the hydrocarbon exhaust portion (Bureau of mines), the effect of fuel additives on catalyst performance (The Dow Chemical Co.), the effect of fuel additives on exhaust visibility (Cornell aeronautics lab) and development of a model for fuel additive emissions determinations (Dow Chemical Company).

As a result of this study, and prior work done on the collection and analyses of particulate emissions, reproducible generation, collection and analysis techniques have been developed. The additives used in this study were a polybuteneamine and methylcyclopentadienyl manganese tricarbonyl. Both additives were used at the levels recommended at the time by the manufacturer, and also at 3 times the manufacturer's recommendation. The polybuteneamine, designated additive A, in this study was used at 1.87 grams/gal, and at 5.61 grams/gal. The manganese additive, designated additive B, was used at .25 grams/gal, measured as manganese, and at .75 grams/gal.

The manufacturer's recommendation for the concentration of this additive has since been reduced.

The engines used on the dynomometer were broken in according to a specified break in procedure and were conditioned for 75 hours using repeated 23 minute federal cycles. Particulate sample was collected from the diluted exhaust (approximately 12 to 1 air/exhaust dilution at a flow rate of 550 cfm diluted). Four filter systems were used to collect particulate from the dilution tube: an Andersen impactor with a 142mm millipore back-up filter at 1 cfm, a 47 mm glass fiber filter at 1 cfm, and two 142 mm glass fiber filters at 1 cfm.

Collections for analyses were made from the dilution tube under steady state (60 mph) conditions, and also using the 23 minute Federal cycle. Collected particulate was analyzed for the following:

Total particulate mass emissions
Mass/size distribution
C, H, N content
Benze-a-Pyrene
Trace elements

In addition, aldehydes, measured as HCHO, and NH_3 were measured from condensed exhaust gas. Specific studies on particulate size and composition were made on selected particulate samples using a scanning electron microscope. Standard gaseous analyses for CO, No_x and unburned hydrocarbons were made on the raw exhaust, primarily as an engine performance monitor.

In addition to the engine dynamometer tests, three vehicles were operated for approximately 17,000 miles on the baseline and the two additive fuels. These vehicles were driven by employees in their normal fashion, and were rotated periodically to eliminate operational variables.

Before active testing was begun on either engine stand or vehicles, an attempt was made at surveying the current fuel additive technology, with hopes of identifying what, if any, future trends were developing. On balance, this attempt was basically unsuccessful. Most research in this area was treated as proprietary, and questions on future additive trends were unvariably answered with "We don't know". A summation of the information which was gathered is in Section VI.

Midway through the contract, an addition was granted for the collection of exhaust gas condensate samples for use in animal health studies. These samples were sent to Dr. Schubik of the Eppley Institute for Research in Cancer, University of Nebraska Medical Center, and were used for research on the effects of exhaust gas on the lung tissue of animals. The condensate samples collected were analyzed, and the data is reported in Section VII.

II. GENERAL CONCLUSIONS

1. Under the conditions used for vehicle and engine stand tests, described in section V, additive concentrations of three times the manufacturer's recommended dosage, when run for 75 hours of repetitive 23-minute Federal cycles, showed the same trend toward increased particulate in the case of additive B as seen in the vehicles using the additive at the recommended level for approximately 17,000 miles. Additive A showed essentially the same trend in the engine runs and in the vehicles, which was no noticeable increase compared to the baseline.

2. The use of repetitive 23-minute Federal cycles on the engine stand with additive fuels did not show significant differences compared to the baseline fuel, with respect to grams/mile particulate, when the additive was used at the recommended dosage. The 75-hour conditioning period is equivalent to approximately 1,500 miles. When total grams/mile particulate were less than .1, any variation beneath that point is considered insignificant since the collection and weighing precision is poor below that level.

3. Chemical analyses (C,H&N) of collected particulate from both the engine stand and vehicles showed variations to the extent that no meaningful conclusions as to the organic content of the particulate can be drawn. In many cases the sample size was so small that any differences could be due solely to the inherent imprecision.

4. In general, the manganese-containing additive, methylcyclopentadienyl manganesetricarbonyl, (Additive B) gave higher grams/mile of emitted particulate than did the polybuteneamine (Additive A) and baseline fuel, in both engine stand and vehicle tests. The increase was from 50% to 100% above the baseline. Additive A was not significantly different from the baseline.

5. Additive A, a metallic additive in general, gave larger particles than the baseline, while Additive B a nitrogenous additive in general gave particulate smaller than the baseline. use of 3 times the recommended concentration did not significantly change the mass medium equivalent diameter, when compared to the recommended concentration.

6. As a result of this study, and prior studies on particulate emissions, a methodology has been developed which can be used to reproducibly generate, collect and analyze particulate emissions. It must be recognized however, that any particulate collection system will entail equipment and technique not currently used for other emissions studies, In addition, any quantitative or qualitative analyses of particulate will require instrumentation and techniques which may not be readily available.

It also must be recognized that any particulate collection system different from the one described in this study may be quite satisfactory for the intended purpose, but cannot be used to compare with particulate mass emissions or particulate size data generated under this study, since the collection system geometry and conditions themselves define the particulate. Comparisons of data generated in a given system should be made with a baseline measured in the same system.

7. The use of the Federal Cycle, 23 minutes or 41 minutes, with unleaded fuel under the conditions described, in general gives such small amounts of collected particulate that qualitative analyses are often meaningless, if not impossible. Steady state conditions (60 mph, collected for 2 hours) will give larger amounts of collected particulate which can be analyzed more thoroughly. The effect of other collection parameters such as temperature, filter face, velocity and collection time is discussed in detail in EPA report APTD-1567, titled "Characterization of particulates and other non-regulated emissions from mobile sources and the effects of exhaust emissions control devices on these emissions".

III. PROPOSED METHODOLOGY

The basic purpose of this study was to build on existing particulate collection and analyses technology, and from this and the additional studies run under this contract, develop a methodology which could be used to generate data for use in fuel additive registration. Under current regulations, the EPA can request data from suppliers of fuel additives relative to the effect of a given fuel additive on emissions. However, in order to allow EPA to make meaningful decisions as to the future registration of these additives, a test protocol must be issued so that data can be generated in a consistent and repeatable fashion. An attempt was made in this contract to build a logical, relatively inexpensive, but thorough method of generating and collecting exhaust particulate emissions, which would allow an effect on particulate emissions due to an additive to be identified.

The details of the particulate collection system which has been set up are covered in section IV, experimental procedures, as well as in previous reports on particulate studies. (APTD-1567: "Characterization of Particulates and Other Non-regulated Emissions from Mobile Sources and the Effects of Exhaust Emission Control Devices on these Emissions". EPA-R2-72-066: "Effect of Fuel Additives on the Chemical and Physical Characteristics of Particulate Emissions in Automotive Exhaust". EHS 70-101: "Development of Particulate Emission Control Techniques for Spark Ignited Engines.)

The engine stand testing in this study consisted of repetitive 23 minute federal cycles. The particulate collection was made during one 23 minute segment, both cold start and hot start. Since the gross amount of particulate collected during one 23 minute cycle is low, the precision of both the mass emission figures and the analytical data is low. In addition, the same engine was used for all the testing and only one 75 hour series of tests was run for each additive concentration. Because of the scatter in data points experienced under normal conditions, the statistical significance of the data is low as far as being representative of an absolute grams/mile figure. However, based on previous work it is felt that the method used for particulate collection is reproducible enough so that any trends which developed as a result of a fuel additive effect are legitimate, even though a statement on the magnitude of the trends would lack statistical significance. An example of a trend which is felt to be meaningful is the increase in particulate mass emissions noted with Additive B after 17,000 miles on the vehicles, and also the increase noted with Additive B when used at 3X the recommended level in the engine stand tests.

Some key conclusions concerning the proposed methodology are as follows:

1. The cost involved in setting up a particulate study such as the one described in this report will be somewhat less than the cost of setting up to do CVS gaseous emissions analyses. Assuming that a suitable structure exists housing either an engine or chassis dynamometer, the cost for setting up the collection system will range from $10,000-$20,000. The most critical cost factor will involve the analyses of the particulate for the various chemical species which might be of interest.

2. A correlation does appear to exist between the engine stand runs of 75 hours continuous 23 minute cycles at 3 x recommended additive concentration, and the 17,000 vehicle tests. Statistically speaking however, this correlation

is of little impact. More statiscally significant is the trend noted in the 17,000 mile vehicle tests.

3. Ambient conditions have a definite effect on particulate emissions collection. Since the operating and collection conditions can be controlled easier for engine tests than they can for vehicle tests, engine stand tests would tend to give data with less scatter. However, a statistically significant fleet test can be set up utilizing 8-10 total vehicles and the scheduling of tests can be made in such a way that only one collection system would be necessary. The effect of different ambient conditions would then be somewhat lessened in a comparison of test vehicles against a baseline.

Following is a discussion of ways in which the tests can be run and equipment necessary to gather the appropriate data. More detail on procedures and techniques is in section IV.

A. EQUIPMENT

The equipment which was used in the experimental work by Dow is described in Section IV. The key parts of the equipment package needed for this methodology are the dilution tube and sampling devices. In general, the geometry of the dilution tube is not critical, although the total flow through the tube should be about 550 cfm. The diameter of the tube should be from 16-18 inches. With a smaller diameter the residence time in the dilution tube will be low, velocity high, and the temperature will be so high that particulate measurements of any meaning will be difficult.

For consistent and reliable particulate sampling, the following steps must be observed:

1. Four sampling probes, each sized to allow a 1 cfm sampling rate of dilute exhaust from the dilution tube, should be installed. The four probes allow to check repeatability within the same test and also permits the use of different types of filter media within the same test run. In addition four filters give more particulate for analytical purposes.

2. The sample probes must be water jacketed to allow the temperature of the dilute exhaust to be maintained at 100°F at the filter.

3. The filters to be used are described in detail in Section III-B along with a description of the Andersen samplers.

4. The filter media used, both Gelman glass fiber and millipore, should be from the same batch for any series of runs. The millipore filter is used for mass emission measurements, as well as true metal analyses. The glass fiber media is for organic measurements.

5. A baseline for the measured particulate must be established using the same engine, base stock fuel, and filter paper batch each time an additive is to be tested.

The engine used for this testing was a 1972 Chevrolet 350 CID V-8. Although a variety of engines could undoubtedly be used, assuming a consistent baseline is established, it is recommended that the 350 Chevrolet be specified. This will allow for easier correlation of data between testing facilities.

The engine should be broken in using the procedure outlined in Table I, Section IV. Low lead gas was used to insure that during the break-in procedure the engine was given enough octane valve lubricity.

After break-in, the engine should be partially dismantled, any combustion chamber deposits removed, and the condition of the valves and cylinders noted. The engine was then reassembled according to manufacturer's specifications.

Before any testing is to be done, the engine must be subjected to a blowby test as described in Table 3 Section IV. If the CFM blowby, after conversion to standard conditions, is higher than an established baseline, a standard leak-down test should be conducted, and the engine should be corrected to meet manufacturer's specifications before proceeding with the testing.

To eliminate any variables, during the engine stand studies, an original equipment exhaust system should be used. This consists of the crossover pipe, exhaust pipe, muffler, and a length of straight tail pipe corresponding to the length of tail pipe used in the vehicles included under this study.

For testing purposes, the engine must be equipped with the same turbo-hydromatic 350 automatic transmission, which is the unit used in vehicles containing the 350 CID Chevrolet engine. This reduces any variables which might result from transmission differences.

Any dynamometer with the capability of handling the loads necessary in the 23 or 41-minute Federal cycle can be used. The important aspect of the dynamometer is its ability to run continuous 23-minute cycles. During the Dow work, a mode monitor system manufactured by Northern Ampower Corporation, was used to control the dynamometer. The Federal cycle was transcribed from the Federal register onto Mylar computer tape. The program was written such that after one 23-minute cycle the engine would idle until the computer had reset itself to run another cycle.

B. PROCEDURE

In attempting to develop a screening technique for fuel additives which could be run on an engine stand, in a relatively short period of time, and would correlate to a mileage accumulation of about 15,000 on a vehicle, the idea of running continuous high speeds on the engine stand for one week or more was ruled out since this type of operation would be non-typical of normal driving. In addition, seven days of around the clock operation at 60 mph would only be 10,000 miles. The approach finally settled on was to take the Federal 23-minute cycle, which contains all commonly encountered modes of operation and continuously cycle the engine. From prior work it had been determined that about 75 hours was sufficient to reach a stabilized situation with respect to particulate emission, for a given additive. As a result of the experimental work reported in Section V, the procedures outlined below are suggested as a screening technique for fuel additive effect on particulate emissions.

1. The continuous 23-minute cycles are to be run for 19 hours each day. This was done by starting the engine at 10:00 a.m. on a given day, and shutting it down at 5:00 a.m. the following morning. A cold start test is to be run when the engine is restarted at 10:00 a.m. After four 19-hour cycling periods, the engine is to be allowed to stand for 12 hours before running the final cold start. After the final cold start, two or more hot starts are to be run. If the amount of particulate collected during the hot or cold start is too low for detailed chemical analyses, a 2-hour 60 mph steady-state run should be made following the last hot start.

2. The test sequence should involve a baseline run of 75 hours for each additive tested, unless several additives are to be done within a short time period. If this is the case, baseline runs should be interspersed between the additive runs as follows:

Additive at recommended concentration

Additive at 3 times recommended concentration

Engine tear-down, clean-off deposits, then baseline run

Additive at recommended concentration

Additive at 3 times recommended concentration

If three or more additives are to be tested, each additive series should be separated by a baseline run.

3. The runs involving additive concentrations three times the recommended level are necessary to amplify the effect of the additive on particulate emissions. While it was recognized that using a given additive at greater than recommended levels could cause other exhaust abnormalties, the experimental work on the two additives in question showed that the vehicles correlated well with the increased additive concentration.

C. PARTICULATE ANALYSES

The analytical procedures described in Section IV should be used to determine the basic chemical make-up of the particulate. In addition, the grams/mile emission rate should be calculated as described in Section IV.

It is recognized that additives of varying chemical composition can be expected to give particulate emissions containing those chemicals, of modifications. This is especially true for additives with inorganic components. Specific analytical techniques for the determination of the quantity and form of these elements are necessary. No attempt was made in this contract to develop techniques for compositions other than those outlined in Section IV and discussed in Section V.

IV. EXPERIMENTAL PROCEDURES

A. PARTICLE GENERATION

1. Engine Dynamometer Studies

The test engine was completely disassembled, cleaned and reassembled according to manufacturer's specifications. It was then mounted on the dynamometer bed plate and attached to a fully instrumented General Electric dynamometer. Appropriate control and sensing devices were attached to the engine. A 1972 350 CID Chevrolet engine was used for all engine tests. It was equipped with standard emission control devices for that model and year. The following procedure (Table 1) was then employed to run-in the new engine, using Indolene .5 cc TEL/gal. fuel.

TABLE I
NEW ENGINE BREAK-IN PROCEDURE
(28 hours)

1) Warm up engine to 180°F coolant outlet temperature at 1000 rpm, no load, set spark advance, timing, and idle according to manufacturer's specifications.
2) Run one hour at 1500 rpm, no load, automatic spark advance and fuel flow. Shut down, retorque cylinder heads, drain and change lubricating oil.
3) Run Cycle 1

RPM	Man. Vac. (In. Hg)	Time (hr.)
1500	15.0	1.0
2000	14.0	1.0
2400	14.0	1.0
2600	14.0	1.0
2000	11.0	1.0
		5.0

4) Run Cycle 2

RPM	Man. Vac. (In. Hg)	Time (hr.)
1500	7.0	0.2
2000	7.0	0.6
2500	7.0	1.0
3000	7.0	1.0
2000	7.0	0.2
		3.0

5) Repeat Cycle 2.

6) Run Cycle 3

RPM	Man. Vac. (In. Hg	Time (hr.)
2000	WOT*	1.0
2500	WOT	1.0
3000	WOT	1.0
3500	WOT	0.5
2800	WOT	0.5
		4.0 x 4 cycles = 16 hours

*WOT - wide open throttle

7) While engine is hot, run motoring compression and conduct leak-down check.

The engine was removed from the dynamometer, drained, partially dismantled, cleaned, reassembled, and placed back on the dynamometer stand. A typical vehicle exhaust system for the specific test engine was attached to one bank of cylinders. The other bank of cylinders was attached to the dynamometer cell exhaust system. Suitable engine monitors were attached to the engine in order to provide continuous monitoring of oil pressure and temperature, coolant temperature, carburetor air flow rate (using a Meriam Laminar Flow Element 50MC-2-45F) and temperature, etc.

After the break-in procedure, the engine was run, with transmission, using repetitive 23-minute Federal cycles. The engine was operated for approximately 75 hours, with one 5-hour shut-down in each 24-hour period. The engine was monitored during this period by performing gaseous analyses, sampled from the Dow dilution tube, during the course of one 23-minute cycle.

At the termination of the test run, the engine was removed from the dynamometer stand, dismantled, and samples for analysis were removed. The engine was completely cleaned, reassembled, and reinstalled on the dynamometer stand.

Subsequent tests did not require the break-in procedure noted in Table 1 unless a new engine was used. If the same engine was used again, the next test series began with the running of the repetitive 23-minute cycles discussed above.

2. Chassis Dynamometer Procedures

A Clayton CT-200-0 chassis dynamometer with a variable inertia flywheel assembly was used in all tests conducted under this program. A Chelsa direct-drive Model PLDUP-200A fan was located in front of the test vehicle, and operated at 1750 rpm providing 18,750 scfm air flow. In these tests, the vehicle was operated under approximately 60 mph road-load cruise conditions (2250 rpm - 17" Hg manifold vacuum) and under cyclic conditions of the Federal Test Procedure (1970) and LA-4 (1975) procedure driven by a vehicle operator following the cycle on a strip-chart recorder driver aid.

Table 2 indicates specific procedures employed to prepare each vehicle for test run.

TABLE 2

VEHICLE TEST PROCEDURE - CHASSIS DYNAMOMETER

1) General Vehicle Inspection

Exhaust System:

a) Inspect for holes or cracks, dents, and collapse
b) Inspect for leaking joints

Engine check

a) All fluid levels
b) All coolant hoses
c) Air pump fan, power steering, and belts
d) Check heat riser (if applicable) for fullness of operation
e) Check automatic choke operation and adjustment

2) Engine Analysis and Tune-up

Leak-Down Test

a) Remove all spark plugs
b) Determine percent leak-down of each cylinder
c) Install recommended, new, and gapped spark plugs, points, and condenser

Scope Check

a) Start engine and allow to warm up for at least 15 minutes
b) With engine running at fast idle, check
  .Spark plugs
  .Spark plug wires
  .Distributor cap and rotor
  .Coil output
  .Points
c) With engine running at idle, check
  .Dwell
  .Timing
d) With engine running at 1500 and 2400 rpm, check
  .Timing advance
e) Carburetor Adjustment
  .Tighten intake manifold and carburetor
  .Install new air cleaner element
  .With engine running at specified idle speed, adjust air to fuel ratio to specifications
  .Make final adjustment on idle speed
f) Recheck all scope patterns for normal appearance

3) Instrumentation and Equipment Installation

Thermocouples - install thermocouples in

a) Engine oil - dipstick
b) Coolant - upper radiator hose engine out
c) Carb air - air filter element

Vacuum and rpm monitors

a) Attach tachometer to ignition coil
b) Connect "U" tube monometer to intake manifold
c) Install throttle cable (if running under cruise mode)

Wheels

a) Remove rear wheels
b) Install test tires and wheel assemblies to insure safe operation

4) Procedure for Cold, Hot Starts, and Engine Temperature Stabilization

Cold Start

a) Place vehicle on the dynamometer rolls, set inertia weights for specific vehicle, and go through the preparation for test as well as the tune-up procedure.
b) Allow at least a 12-hour soak period.
c) Connect vehicle tailpipe to dilution tube.
d) Start the vehicle and proceed with the individual test.

Hot Start

The hot start procedure is the same as for the cold start except that the vehicle was warmed up and allowed to sit for 10 minutes before starting.

Engine Temperature Stabilization

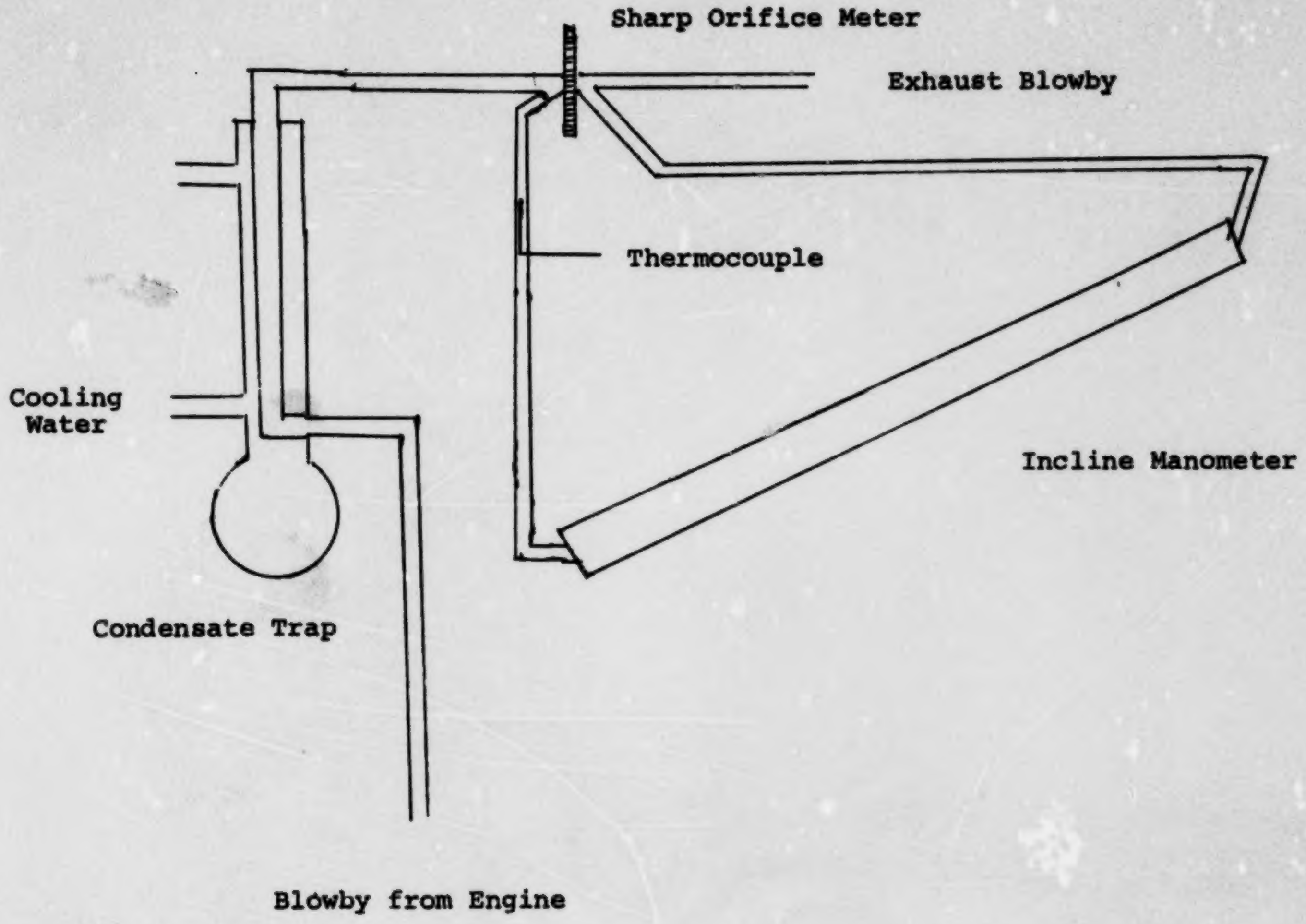
Upon completion of the tune-up procedure (Step 2) the vehicle is started cold and driven a total of 32 highway miles at 60 mph to allow the engine temperature to stabilize. The vehicle was then driven on-to the dynamometer rolls (Step 3) and prepared for the test during which time the engine idles for approximately five minutes. When preparation has been completed, the vehicle was placed in gear and the speed was increased to 2250 rpm and the intake manifold vacuum was set at 17.0" Hg by controlling the amount of load imposed on the drive wheels. At the time, when the load and the speed become stabilized, the tailpipe is connected to the dilution tube inlet pipe and sampling is started.

Table 3 is a description of the blowby test procedure used to ascertain that proper piston ring and valve guide seating is occurring.

TABLE 3
BLOWBY TEST PROCEDURE
Clayton CT-200 Chassis Dynamometer Used

1) Thermocouples installed as follows to record accurate temperatures:
    a) Top radiator hose
    b) Carburetor venturi
    c) Oil pan
    d) Ambient air
    e) Blowby gas flow tube
2) Close oil dip stick tube
3) Close rocker cover vent to carburetor (right side on 350 CID Chevrolet)
4) Install tube from PCV (left side) to sharp orifice meter intake (1/4" port) Figure 1
5) Install Vernier band throttle
6) Place wind fan in front of car
7) Connect accurate tachometer
8) Connect blowby apparatus as follows (see diagram for details):
    a) Use cooling water to maintain 75-85°F blowby
    b) Connect condensate trap to tube from PCV
    c) Connect outlet from condensate trap to sharp orifice meter (use 1/4" orifice)
    d) Connect incline water monometer across orifice meter
    e) Connect mercury monometer to engine vacuum

Figure 1. BLOWBY TEST APPARATUS


Sharp Orifice Meter
Exhaust Blowby
Thermocouple
Cooling Water
Incline Manometer
Condensate Trap
Blowby from Engine

9) All test run at 2000 rpm

10) Collect the following data at each load condition:

    a) MPH
    b) RPM (maintain at 2000)
    c) Load
    d) Intake manifold pressure
    e) Ambient air
    f) Carburetor air
    g) Coolant temperature
    h) Oil temperature
    i) Barometer reading
    j) Wet and dry bulb temperatures
    k) Blowby temperature before orifice meter
    l) Pressure drop observed across water monometer
    m) Observed cfm blowby - read from sharp orifice meter chart relating pressure drop to cfm

11) CFM at standard conditions is calculated using a cfm correction factor to compensate for barometric pressure and a standard conversion factor to bring the final result to cfm at standard conditions.

12) The initial reading is taken at the lowest horsepower load measurable. Subsequent readings at multiples of 10 hp.

13) See attached data collection sheet for an example of one blowby run.

B. PARTICLE COLLECTION

Exhaust particles were collected after air dilution of the exhaust in the large dilution tube described below. During the engine stand studies, one-half of the engine exhaust was fed into the tube while the other half was exhausted through the dynamometer cell exhaust system. With vehicles, the entire exhaust stream was diluted.

1. Dilution Tube

Air dilution and cooling of the exhaust was accomplished by a dilution tube 16 inches in diameter and 27 feet in

BLOW BY MEASUREMENTS

Figure 2

SHEET NO. 34

OBSERVER WT DATE July 10 - 1973
VEHICLE MAKE Chevrolet YEAR 1972 NUMBER D2549
MILES ON VEHICLE 16.352 DISPL. 350 NO. OF CYL. V8 C.R. 8.5.1
IGNITION TIMING 6° AT 600 RPM CARB RP BBL 2
TRANSMISSION 350 Th VAC. IDLE ______ HP ______ RPM ______
BAROMETER IN Hg 29.40 at 82 WET BULB 66.0°F DRY BULB 82.0
CORRECTED BAROMETER(DRY) 28.79 at 28.5°F ABS. HUMIDITY .470 GR/LB
INERTIA WEIGHT 4500 LBS
VALVE COVER PRESSURE ± 0"
SPARK PLUG TYPE R44T DWELL 30° HP ______ RPM ______
REMARKS: CORR WET BAR = 29.26

BLOW-BY MEASUREMENTS TEMPERATURES

SPEED	57	56	55	53	52	
RPM	2000	2000	2000	2000	2000	
LOAD	3.4	10	20	30	40	
ENG VAC.	18.9	17.5	15.0	11.0	8.3	
AMB. AIR	90	97	98	99.	99	
CARB. AIR	118	120	120	120	122	
WATER	206	208	212	214	222	
OIL	242	246	250	256	265	
BLOW-BY AIR	85	85	85	85	85	
OBS. PRESS DROP	.65	.86	1.38	200	2.42	
OBS. CFM	.65	.81	1.01	1.23	1.35	
CFM CORR. FACTOR	.9963	.9963	.9963	.9963	.9963	
CORR CFM	.647	.807	1.006	1.225	1.345	
STD. CONV. FACTOR	1.078	1.078	1.078	1.078	1.078	
CFM at STD COND.	.697	.869	1.084	1.320	1.449	

length constructed of extruded polyvinyl chloride (PVC), except for a 6' stainless steel inlet Section, in several sections with butt joints which were taped during assembly prior to each run (Figure 3). The diluent air coming into the tube is filtered by means of a Dri-Pak Series 1100 Class II PIN 114-110 020 untreated cotton filter assembly. This filter assembly is 24" x 24" and has 36 filter socks which extend to 36 inches in length. This filter will pass particles 0.3μ in size and smaller. Pressure drop at 600 cfm flow rate was minimal.

Exhaust was delivered to the tube via a tailpipe extension which was brought into the bottom of the tube downstream of the dilution air filter assembly. The extension was bent 90 degrees inside the tube, thus allowing the introduction of the exhaust stream parallel to the tube axis. Within the dilution tube, along the perpendicular plane of the end of the exhaust extension was a mixing baffle which has an 8-inch center hole and was attached to the inside diameter of the tube. The baffle presented a restriction to the incoming dilution air in the same plane as the end of the exhaust extension and performed three essential functions.

a. Provided a turbulent mixing zone of exhaust gas and dilution air.

b. Eliminated engine exhaust pulsations in the tube.

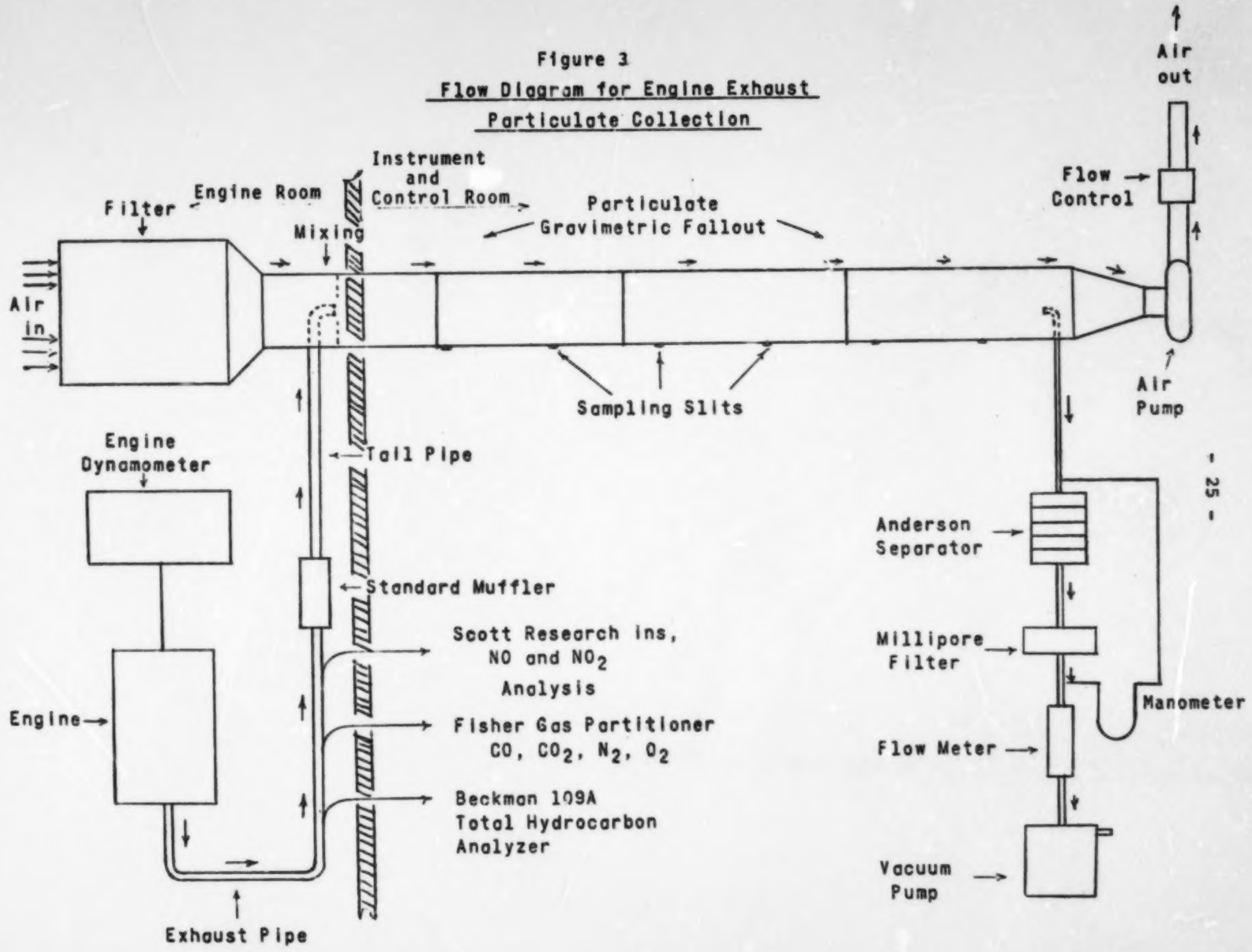
c. Caused the tube to perform as a constant volume device over a wide range of engine exhaust output volumes.

2. Sampling Devices

The particulate sampling zone for particles smaller than 15μ was located at the exhaust end of the dilution tube. Four isokinetic sample probe elbows are located in the ex-

Figure 3

Flow Diagram for Engine Exhaust Particulate Collection


Air out
Flow Control
Instrument and Control Room
Engine Room
Filter
Mixing
Particulate Gravimetric Fallout
Air in
Air Pump
Sampling Slits
Engine Dynamometer
Tail Pipe
Standard Muffler
Engine
Scott Research ins, NO and NO_2 Analysis
Fisher Gas Partitioner CO, CO_2, N_2, O_2
Beckman 109A Total Hydrocarbon Analyzer
Exhaust Pipe
Anderson Separator
Millipore Filter
Manometer
Flow Meter
Vacuum Pump

haust-air stream. One probe is connected to an Andersen Impact Sampler Model 0203, a filter assembly, and a vacuum pump, in that sequence. The probes are 0.754 inch ID stainless steel tubes which are located as shown in Figure 1. A mercury manometer was connected between the dilution tube probe and the exhaust side of the filter assembly, to measure the pressure drop across the filter. A flow meter was used to monitor and regulate the flow through the Andersen Sampler during the course of each run. Two other sample probes, each were connected to 1 cfm Millipore filter holders (142 mm) fitted with Gelman Type A glass fiber filter pads and vacuum pumps. The fourth filter was a 47 mm, 1 cfm glass fiber.

Prior to use, all the filters were stored in the instrument room which was temperature- and humidity-controlled. The filters were placed on the tray of the Mettler Analytical Balance, allowed to reach equilibrium, and then weighed out to 0.1 milligram (mg).

After the test, the filters were removed from the holders and again allowed to reach equilibrium, noted by no further change in weight, and then weighed to 0.1 mg. This was done in the same room in which the papers were stored. The Millipore filter pads used were 142 Type AAWP 0.8μ. The glass fiber filter pads used were Gelman 0.3μ Type A. It is extremely important that all filters used in a given sequence of tests be from the same batch. Variations in batch lots have been found to lead to gross differences in collected particulate.

Andersen Sampler Model 0203 with a back-up 142 mm Millipore filter was used as the basic particle collection device for determining mass size distribution. Sample probes sized to deliver an isokinetic sample from the dilution tube were connected to the Andersen Sampler through which a proportional sample was drawn at 1 cfm. The D_{50} cut-off values for the

Andersen stages are listed in Table 4. The D_{50} value is the size at which 50% of those particles are collected, while the remaining 50% pass on through to be collected on the next stage.

TABLE 4

D_{50} VALUE - ANDERSEN MODEL 0203

Stage 1	D_{50} 9μ
Stage 2	D_{50} 5.45μ
Stage 3	D_{50} 2.95μ
Stage 4	D_{50} 1.55μ
Stage 5	D_{50} 0.95μ
Stage 6	D_{50} 0.54μ

Preweighed glass collection plates were used in this study. Back-up filters were either Millipore Type AAWP 0.8μ or Gelman 0.3μ Type A 142 mm diameter. Gelman glass fiber filters were routinely used while the Millipore filters were used for special analytical applications. Particulate larger than 15μ was collected as gravimetric fallout in the dilution tube.

C. CONDENSATE COLLECTION

Exhaust gas condensate was collected for aldehyde and NH_3 analyses. A tap was placed into the raw exhaust gas stream, as close to the tailpipe of a vehicle as practical (about 12 inches in most cases) and 8 feet from the muffler in an engine run. Raw exhaust was drawn through a three-stage cold trap at the rate of 1 cfm. The cold trap consisted of three flasks connected in series containing 40 grams each of DI water, immersed in an ice water bath. The exhaust gas flow bubbles through the water in the flasks. Condensate was collected for 41 minutes during a modified Federal cycle cold start, and for 23 minutes during a Federal cycle hot start. Sampling was terminated at 25 minutes during a steady-state run.

The condensate from the exhaust gas was analyzed for ppm of HCHO and NH_3. It was felt desirable to express this analysis in volume percent to compare to the other components analyzed in the exhaust gas. The procedure for this calculation is as follows:

The "Ideal Gas Law" was used

$$PV = n\,RT$$

$$V = \frac{n\,RT}{P}$$

The total liters of exhaust that was put through the condenser is known, the liters of the aldehyde can be calculated from the formula above, so the volume percent can be calculated. This volume percent is reported as volume parts per million in the exhaust.

D. ANALYTICAL METHODS

Collected exhaust particles have been analyzed for both physical and chemical character. Many analytical techniques have been employed in the past, some of which provide very similar data in the interest of correlating trends observed. This section reviews the basic analytical concepts applied to each of the many test components from fuels to exhaust particles. Detailed descriptions of the specific analytical procedures employed are then presented. Table 5 is a summary of the techniques used on the exhaust emissions.

TABLE 5
ANALYTICAL TECHNIQUES FOR EXHAUST SPECIES

O_2, N_2, CO, CO_2	Fisher Gas Partitioner
Total Hydrocarbons	Beckman Model 109A Flame Ionization Detector
Oxides of Nitrogen	Beckman UV and IR Analyzer
C, H	Pyrolysis
Benzo-a-pyrene	Chromatograph, Fluorescence
Trace Metals	Emission Spectroscopy, Atomic Absorption
Aldehydes	Polarography
NH_3	Steam Distillation, Titration

1. Fuels

Each test fuel was analyzed to verify concentrations of additives under study. Additionally, complete physical analyses were determined on the base stock test fuel. These analyses include distillation, octane numbers, fluorescence indicating analysis (FIA) composition, Reid vapor pressure (RVP), and trace metals. The test fuel was Indolene O, and was from the same batch for all engine and vehicle runs. The additive blending was done in a large batch, and the fuel was then drummed off for future use.

2. Oils

Engine oils were examined for trace metals both before and after test runs. Compliance of physical properties with specifications was verified. The oils were only checked on the engine stand runs, not on vehicles.

3. Diluent Air

Mass and composition of the filtered diluent air particulate was determined with the engine or vehicle operating in the air pick-up zone as during a test run. This data was necessary to provide a correction factor applicable to the mass emission rates determined during a test run.

4. Exhaust Gases

Engine exhaust gases were analyzed routinely several times during the conditioning sequence and during sampling runs. Schematically, exhaust gas sample points are as shown earlier in Figure 1. The engine exhaust gas was analyzed for oxygen, nitrogen, carbon monoxide, carbon dioxide, and total unburned hydrocarbons. The hydrocarbons were broken down into saturates and unsaturates. These analyses were done by gas chromatography, chemical absorption, and a total hydrocarbon analyzer. Data reduction was via an IBM 1800 computer through a Bell Telephone ASR 33 Teletype interface.

a. Analytical Equipment

A Fisher Gas Partitioner was used for the analysis of oxygen, nitrogen, carbon monoxide, and carbon dioxide. The partition column consisted of a 6-foot section containing hexamethyl phosphoramide and a 6 1/2-foot section containing 13x molecular sieves in series.

Total hydrocarbons were obtained from a Beckman Model 109A Total Hydrocarbon Analyzer. The concentration of unsaturated hydrocarbons was determined by passing the sample through an absorption tube (1/2" x 8") filled with 30-60 mesh pink Chromosorb impregnated with 50 percent mercuric perchlorate. The output of the gas chromatograph was coupled with a Hewlett-Packard Model 3370A Digital Integrator which has an ASCII coded output to drive an ASR 33 Teletype and punch paper tape.

b. Sampling

A Neptune Dyna-Pump was used to pull the sample from the exhaust pipe sampling point through 1/4" OD stainless steel tubing and transfer it to the total hydrocarbon analyzer and the gas sampling valve of the gas chromatograph through 1/8" OD stainless steel tubing. A manifold system was provided to allow the operator to calibrate the equipment with the appropriate standards.

c. Standardization

A gas mixture containing known concentrations of oxygen, nitrogen, argon, carbon monoxide, carbon dioxide, and n-hexane was used as a reference standard for the total hydrocarbon analyzer and the Fisher Gas Partitioner.

d. Operation

The operator typed the proper computer code and program number on the teletypewriter, injected the reference standard, and pressed the integrator start button. As the peaks emerged, the time and area information was encoded and stored on punched paper tape. Each succeeding exhaust gas was identified along with the total hydrocarbon level, and run in the same manner as the standard. When the series was finished, the punched tape was sent to the computer by teletype over regular telephone lines.

e. Data Reduction

A typical output format for the gas analysis is shown in Figure 2. Identification of the components in the standard was based upon each peak size in descending order. Estimated retention time was the updated time of each peak in the standard. Retention time windows are 4 seconds plus 2 percent of the retention time. Actual percent is a direct ratio of the area counts in the unknown sample to the area counts in the standard times the volume percent in the standard. The total percent actual will normally be 97-98 percent since water is removed from the saturated sample after the sampling valve.

A correction for the unresolved argon in oxygen was made based upon response factors and the amount of argon found in a number of exhaust gas samples by mass spectroscopy.

The actual percent was normalized to 100 percent in the next column on a moisture-free basis, and an Exhaust Gas Analysis report was issued (Figure 2). The air-to-fuel ratio was calculated from this analysis, the total hydrocarbon content, and the percent carbon in the fuel.

5. Oxides of Nitrogen

a. Equipment

Beckman Ultraviolet Analyzer
Beckman Infrared Analyzer

Figure 4

```
G. C. ANALYSIS - TECHNICAL DATA -                    10-16-70
GOV RUN 23 OCT 16
CYCLE 2 72.9 HOURS
HC 620.

 PEAK      TIME          PCT. VOL.         COMPOUND
  NO.  ACT.    EST.   ACTUAL    NORM.   IDENTIFICATION


   1    22.     21.    0.000    0.000   COMPOSITE
   2    59.     59.   12.003   12.366   CARBON DIOXIDE
   3    83.     83.    1.493    1.538   OXYGEN
                       0.900    0.927   ARGON
   4   104.    107.   81.033   83.492   NITROGEN
   5   187.    188.    1.626    1.675   CARBON MONOXIDE
                     -------  -------
                      97.060  100.000   TOTALS
                       2.940            BALANCE BY DIFFERENCE
                       2.940            TOTAL CONTAMINATION LEVEL

--------------------------------------------------------------
--------------------------------------------------------------

         EXHAUST GAS ANALYSIS            10-16-70

GOV RUN 23 OCT 16
CYCLE 2 72.9 HOURS
HC 620.

 TIME  PERCENT  IDENTIFICATION

  83.     0.9   ARGON
 107.    83.5   NITROGEN
  83.     1.5   OXYGEN
 188.     1.68  CARBON MONOXIDE
  59.    12.4   CARBON DIOXIDE
        -----
        100.0   TOTAL

FRACTION CARBON IN FUEL 0.8625

TOTAL HYDROCARBON CONTENT  620. PPM.

AIR/FUEL RATIO 14.8
```

Recorder - Texas Instrument Company

The above pieces of equipment were in a single, self-contained unit built by Scott Research Labs Inc., San Bernardino, California.

b. Calibrating Gases

Nitric oxide (3545 ppm in nitrogen)
Nitrogen dioxide (862 ppm in nitrogen)

These standard gases were purchased from Scott Research Labs Inc.

Nitrogen was used as zero calibrating gas.

c. Procedure

Before making NO, NO_2 measurements, the paper filters (Whatman #3) to each analyzer were changed and the Drierite dryer in the exhaust sample line was replaced. Both analyzers were standardized using the appropriate calibrating gas at a constant flow. The zero standardizing was done using nitrogen as the calibrating gas and using the same flow rate.

After the instrument was standardized, the exhaust gas was passed through the analyzer using the same flow rate as in the standardization step. The NO, NO_2 values were recorded by the dual pen Servo-riter recorder. Figure 3 indicates the source of the exhaust gas sample.

6. Exhaust Particles

The collection and classification techniques employed allow the calculation of mass emission rates in grams/mile of exhaust particulate. Additionally, cumulative mass distribution data can be calculated. Several collection methods were used, and have been discussed previously in Section III-B, page 13.The specific techniques for chemical analysis of this particulate matter are discussed in this section.

a. Carbon and Hydrogen

The percentage of carbon and hydrogen in the particulate was determined by pyrolysis and collection of the combustion products. An entire 142 mm glass fiber filter containing the particulate was placed in a large platinum boat. The boat was then transferred to a combustion tube, and the sample was combusted at 1100°C for 3/4 hour. Carbon dioxide and water were absorbed in micro absorption tubes and weighed in the conventional manner. The C and H values were then calculated from the increase in weight using the given weight of the particulate.

In general, this technique is quite accurate for carbon and hydrogen analysis. However, the small sample sizes generated in a 23-minute cycle or from vehicles or engines operating on unleaded fuel make it difficult to obtain precise results. For example, the 142 mm Gelman glass fiber filters have a blank of approximately 7 mg for hydrogen and a spread of nearly 1 mg. For carbon the blanks are over 2 mg with a spread of 0.5 mg. It is not uncommon to have sample sizes of less than 2 mg; therefore, the inherent inaccuracy of weighings (even using a 5-place balance) plus the large blank size make the results of a small sample only meaningful in a gross comparative sense.

This technique can be used on samples collected on the Andersen Sampler plates by careful transfer of the particulate to the combustion chamber. However, even with the best handling techniques the transfer of particulate is only about

30 percent. In general, engine runs in which very little sample was collected on the filter pads also gave very little on the Andersen Sampler Plates.

Nitrogen can also be determined by pyrolysis, but due to the small sample size no meaningful results have been obtained in nitrogen content.

b. Benzo-α-pyrene

Samples of exhaust particulate were collected on Gelman 142 mm glass fiber filter pads in a Millipore filter holder operating at 1 cfm. Particulate weights gathered in this fashion ranged from 0.2 to 35 mg. The samples on the glass fiber filter pads were analyzed for benzo-α-pyrene in the following manner.

When available a sample of at least 10 mg (on either one or two filter papers) was used for analysis. The filters were folded and rolled with the particulates toward the inside of the roll and tied with copper wire. The rolls were Soxhlet extracted for at least 6 hours (with siphoning four to six times per hour) with 75 ml of benzene. The extracts were evaporated under a stream of filtered air at room temperature to approximately 3 ml. This concentrate was filtered through a M-fritted glass filter into a tared vial. The flask and filter were washed three times with approximately 2 ml of benzene for each wash. The combined filtrates were evaporated to dryness at room temperature with a stream of filtered air.

The residues obtained from both sample and blank filters were weighed and the difference between them designated "benzene soluble weight" for each sample. The residue was dissolved in 0.2 ml of methylene chloride and a 10-40 μl aliquot was spotted in 2 μl increments on a pre-conditioned Alumina TLC plate along with a known standard of benzo-α-pyrene in methylene chloride. The TLC plates were conditioned by heating at 120°C for 1.5 hours and desiccating overnight in a 45 percent relative humidity chamber (saturated aqueous zinc nitrate). The TLC plate was developed in an unsaturated tank containing 20 ml of ethyl ether in 200 ml of n-pentane to a height of 15 cm (approximately 45 minutes).

The benzo-α-pyrene spots were identified by comparison of R_f's with that of the standard spot under an ultraviolet lamp. The spots, marked with a pencil, were circumscribed with a #15 cork borer and scraped from the plate into vials. All TLC work was performed as much as possible in a dimly lighted area to avoid decomposition of the benzo-α-pyrene.

Five ml of 5 percent acetone in n-pentane was added to the alumina in the vial and it was agitated for 15 minutes on a mechanical shaker. The slurry was filtered through an F sintered glass filter into a vial, washing the alumina four times with approximately 2 ml of 5 percent acetone in n-pentane with a 45-second soak period between each wash. The combined filtrates were evaporated to dryness at room temperature using a stream of filtered air. The benzo-α-pyrene residue was taken up in 2.0 ml of concentrated sulfuric acid. This solution was evacuated for five minutes to remove trapped air bubbles and its fluorescence was measured in a one-cm cell at 540 nm while exciting at 470 nm on an Amino-Bowman Spectrophotofluorometer using a #4 slit arrangement and a sensitivity of 30.

Standard and blanks were carried through the entire TLC procedure. The blanks were subtracted from all fluorescence readings and the net fluorescence values for each sample were used to calculate the amount of benzo-α-pyrene present. Throughout all steps in the procedure the samples were refrigerated when not actually being processed and exposure of the samples to light was kept at a minimum.

c. Trace Metals

Both emission spectrometry (ES) and atomic absorption (AA) were used for determination of metals in the particulate. Atomic absorption was primarily used for lead determination. Trace metals were determined by ES on Millipore filters while lead was determined as a percent of the particulate collected on the 142 mm, 1 cfm fiberglass filter.

1) Emission Spectrometry

a) Principle

Organic matter in the sample is destroyed by wet ashing in sulfuric, nitric and perchloric acids. The resulting solution is taken to dryness and the residue is taken up in a spectroscopic buffer solution containing the internal reference element, palladium. A portion of the solution is dried on pure graphite electrodes. The electrodes thus prepared are excited in an a.c. arc discharge and the spectrum is photographed. The intensity ratios of selected lines are determined photometrically and the concentration of each element is read from an analytical curve relating intensity ratio to concentration.

b) Apparatus

(1) Excitation. Excitation is obtained by the use of a 2400 volt a.c. arc discharge - Jarrel-Ash Custom Varisource, or equivalent.

(2) Spectrograph - Baird 3 meter grating spectrograph. Reciprocal dispersion is 5.55 A/mm in the first order.

(3) Developing equipment - Jarrel-Ash Company. Plates are developed in a thermostatically controlled developing machine, washed and dried over heat in a stream of air.

(4) Densitometer. Spectral lines are measured with a non-recording projection-type densitometer. Densitometer Comparator, Baird Associates Inc.

(5) Calculating equipment. A calculating board is employed to convert densitometer readings to log intensity ratios. Jarrel-Ash Company.

(6) Wet ashing equipment. A micro Kjeldahl digestion rack is used for wet ashing the organic solvents.

c) Reagents and Materials

(1) Distilled nitric and perchloric acids. Perchloric acid is an intense oxidizing agent. Organic matter should not be heated in perchloric acid unless in the presence of sulfuric or nitric acid.

(2) Sodium nitrate, reagent grade ($NaNO_3$).

(3) Palladium diamine nitrite, $Pd(NH_3)_2(NO_2)_2$.

(4) Water soluble salts of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn.

(5) Electrodes, high purity graphite, 1/4" diameter by 3/4" length. Ultra Carbon Corporation.

(6) Photographic plates - Eastman Spectrum Analysis No. 3.

(7) Kjeldahl flasks, 10 ml.

d) Calibration

(1) 0.2182 gm of palladium diamine nitrite $Pd(NH_3)_2(NO_2)_2$ were dissolved in water. 10 ml of concentrated reagent grade nitric acid were added and the mixture diluted to volume with water in a 100 ml volumetric flask. This solution contains 1 mg Pd per ml.

(2) A buffer solution was prepared by dissolving 20 gm of sodium nitrate in water. 5.0 ml of the palladium solution above and 7.5 ml of concentrated reagent grade nitric acid were added and the whole diluted to 100 ml.

(3) A stock solution containing 0.01% (0.1 mg/ml) each of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn was prepared. Two aliquots of this solution were diluted tenfold and one hundred-fold to provide 0.001% and 0.0001% solutions.

(4) Standard additions of the impurity elements were made to Kjeldahl flasks as shown in Table 6.

(5) 0.5 ml of concentrated reagent grade sulfuric acid was added to the Kjeldahl flasks and the solution evaporated to dryness. After cooling, 1 ml of concentrated nitric acid was added and the mixture was evaporated to dryness again. The residue was taken up in 5 ml of buffer solution, warming, if necessary, to put the salts into solution.

Table 6

Concentration	ml. of standard addition impurity solution		
Blank			
0.00001%	0.5 ml.	0.0001%	solution
0.000025%	1.25 ml.	"	"
0.00005%	0.25 ml.	0.001%	"
0.0001%	0.5 ml.	"	"
0.00025%	1.25 ml.	"	"
0.0005%	2.5 ml.	"	"
0.00075%	0.375 ml.	0.01%	"
0.001%	0.5 ml.	"	"
0.0025%	1.25 ml.	"	"
0.005%	2.5 ml.	"	"
0.01 %	5.0	"	"

Table 7
Analytical Line Pairs

Element	Analytical Line A	Internal Standard Line A	Concentration Range %
Al	3092.71	3027.91 Pd	0.000025-0.0010
Ca	3179.33	"	0.00025-0.010
Cu	3273.96	"	0.00001-0.00025
Fe	3021.07	"	0.0001-0.010
Fe	3020.64	"	0.000025-0.0050
Mg	2802.69	"	0.000025-0.0010
Mg	2779.83	"	0.0005-0.010
Mn	2933.06	"	0.0005-0.010
Mn	2794.82	"	0.00001-0.0010
Ni	3414.77	"	0.000025-0.0010
Ni	3037.94	"	0.0005-0.010
Pb	2873.32	"	0.0010-0.010
Pb	2833.07	"	0.00005-0.0050
Sn	3175.02	"	0.00005-0.0050
Sn	2863.33	"	0.00075-0.010
Zn	3345.02	Background	0.0001-0.010

(6) The end of the 3/4" graphite electrodes was polished on filter paper and placed in a stainless steel drying tray. A drop of kerosene was placed on the top of each electrode to seal the porosity and the electrode allowed to dry. One pair of electrodes was prepared for each of the standard addition solutions by pipetting 0.03 ml of the solution onto the end of each electrode. The electrodes were dried slowly over micro burners in a gas drying oven and stored in a desicator until run.

(7) The samples were excited in water cooled electrode holders using the following conditions:

(a) Current, 4.0 amps, a.c. arc.

(b) Spectral region, 2150-3550 A.

(c) Slit width, 50μ

(d) Electrode gap, 2 mm.

(e) Pre-burn period, 10 seconds.

(f) Exposure period, 90 seconds.

(8) The emulsion was calibrated by use of a stepped filter or by other recommended methods described in the "Recommended Practice of Photographic Photometry in Spectrochemical Analysis" A.S.T.M. Designation: E116, Methods for Emission Spectrochemical Analysis, (1964).

(9) The emulsion was processed according to the following conditions:

(a) Developer (D19, 20.5°C), 3 1/2 minutes.

(b) Stop bath (SB-4), 1 minute.

(c) Fixing bath (Kodak Rapid Fixer), 2 minutes.

(d) Washing, 3 minutes.

(e) Drying, in a stream of warm air.

(10) The relevant analytical line pairs were selected from Table 7 (pg 41). The relative transmittances of the internal standard line and each analytical line were measured with a densitometer. The transmittance measurements of the analytical line pairs were converted to intensity ratios by the use of an emulsion calibration curve and a calculating board.

(11) Analytical curves were constructed by plotting concentration as a function of intensity ratio on log-log graph paper. For best results, the average of at least four determinations recorded on two plates were plotted.

e) Procedure

(1) The available sample was weighed directly into a Kjeldahl flask. Sulfuric acid was not used in the wet ash procedure because test samples usually contained a large amount of lead which would form the insoluble sulfate. Wet oxidation was carried out with nitric and perchloric acid only. Extreme

caution was exercised in the use of this technique. Concentrated nitric acid was added dropwise, a few tenths ml at a time, to the hot mixture to aid in oxidation. A few drops of concentrated perchloric acid may be added to the hot solution after most of the free carbon has been destroyed, to hasten complete oxidation. When the solution became water clear, it was evaporated to dryness. After cooling, 0.5 ml of nitric acid was added and the mixture evaporated to dryness. The addition of 0.5 ml of nitric acid was repeated and the solution evaporated to dryness again. The inorganic residue was dissolved in dilute nitric acid and the volume adjusted to a known concentration, usually 10 mg/ml. If the original sample size was below 30 mg, a less concentrated solution was usually made up. Aliquots of this solution were taken to dryness and then the buffer solution (d2) added in an amount to give a dilution factor of 100x. One sample was analyzed by the direct reader while a second was examined photographically. Some samples had to be run at factors larger than 100x in order to get the concentration for some elements to fall within the range of the analytical curves. By varying the sample to buffer ratio any number of concentration or dilution factors could be achieved. A blank of the acids used was carried through in the same manner as the sample.

(2) Proceed as in d(6), (7), (8), (9), and (10) of the calibration procedure. Duplicate spectra were recorded for each sample.

f) Calculations

The intensity ratios were converted to concentration by use of the analytical curves.

g) Precision and Accuracy

Representative precision and accuracy of the method are given in Table 8. Each of the twelve samples A_1, A_2, A_3, B_1, B_2, B_3, C_1, C_2, C_3, D_1, D_2, D_3, was analyzed by means of duplicate excitation.

2) Atomic Absorption

a) Method for Lead Determination

Following nitric acid digestion, particulate samples were washed into 50-ml volumetric flasks and diluted to mark. This normally put the concentration of lead in the flasks between 20 and 200 μg Pb/ml. If the concentration was higher than 200 μg Pb/ml, the sample required redilution. The samples were analyzed on an atomic absorption spectrophotometer (Perkin-Elmer Model 303) using a hollow cathode lamp with a lead cathode filament. Operating conditions were as follows: 10 milliamps tube current, light path slit opening - 4, ultraviolet light range, acetylene-air oxidizing flame, one-slot burner head, wavelength - 2170 angstroms. The sample solution is aspirated into the flame where lead atoms present absorb the light from the lead cathode filament. The amount of absorbed light is proportional to the concentration of lead. The samples were analyzed in conjunction with the following series of lead standards: 10, 20, 40, 60, 80, 100, 150, and 200 μg Pb/ml. The concentration of the standards was plotted versus their absorbance values giving a standard curve. With the absorbance values for the samples and the standard curve, it was possible to determine the concentration of lead in the samples. The sensi-

TABLE 8

REPRESENTATIVE PRECISION AND ACCURACY OF EMISSION SPECTROSCOPY

Sample	% Al	% Ca	% Cu	% Fe	% Mg	% Mn	% Ni	% Pb	% Sn	%Zn
A_1	0.000044	0.00043	0.000048	0.00043	0.00049	0.00046	0.00047	0.00056	0.00052	0.00040
	0.000052	0.00050	0.000054	0.00055	0.00052	0.00057	0.00055	0.00059	0.00059	0.00045
A_2	0.000045	0.00043	0.000046	0.00044	0.00047	0.00051	0.00045	0.00050	0.00053	0.00054
	0.000052	0.00037	0.000047	0.00043	0.00050	0.00050	0.00051	0.00051	0.00050	0.00040
A_3	0.000041	0.00043	0.000050	0.00046	0.00053	0.00049	0.00047	0.00052	0.00050	0.00052
	0.000052	0.00050	0.000048	0.00046	0.00049	0.00046	0.00048	0.00053	0.00046	0.00042
B_1	0.00012	0.00105	0.00012	0.0010	0.00105	0.0010	0.0010	0.00105	0.0011	0.00094
	0.000097	0.00093	0.00010	0.00094	0.00095	0.0012	0.00096	0.00098	0.00094	0.0012
B_2	0.000097	0.00086	0.000099	0.00090	0.00092	0.0011	0.0010	0.0010	0.00105	0.00125
	0.000094	0.00083	0.000095	0.00105	0.00091	0.00066	0.00105	0.00105	0.00105	0,0010
B_3	0.000082	0.00085	0.000095	0.0010	0.0010	0.00086	0.0010	0.0010	0.00099	0.00096
	0.00011	0.00074	0.000096	0.0010	0.00090	0.00092	0.00105	0.0010	0.0010	0.00115
C_1	0.00028	0.0023	0.00023	0.0025	0.0023	0.00265	0.00245	0.00235	0.00255	0.0014
	0.00030	0.0018	0.00028	0.0030	0.0023	0.00195	0.00265	0.00255	0.0027	0.00215
C_2	0.00020	0.00225	0.00023	0.0023	0.0023	0.00265	0.0023	0.00245	0.00215	0.00225
	0.00023	0.00235	0.00025	0.00235	0.0024	0.00275	0.00245	0.0026	0.0023	0.0030
C_3	0.00024	0.0025	0.00026	0.00275	0.0023	0.00245	0.0026	0.0025	0.0025	0.0030
	0.00028	0.00275	0.00028	0.00285	0.0024	0.0025	0.00255	0.00245	0.00265	0.0020
D_1	0.00074	0.0070	--	0.0055	0.0057	0.0059	0.0055	0.0055	0.0064	0.0058
	0.00064	0.0054	--	0.0053	0.0051	0.0058	0.0058	0.0045	0.0059	0.0050
D_2	0.00059	0.0049	--	0.0057	0.0048	0.0045	0.0056	0.0045	0.0053	0.0050
	0.00063	0.0057	--	0.0059	0.0047	0.0048	0.0057	0.0048	0.0057	0.0050
D_3	0.00059	0.0043	--	0.0050	0.0045	0.0047	0.0050	0.0043	0.0054	0.0037
	0.00053	0.0050	--	0.0055	0.0055	0.0054	0.0055	0.0049	0.0049	0.0041

A_1, A_2, and A_3 contain 0.00005% of Al and Cu, and 0.0005% of each other element. B_1, B_2, and B_3 contain 0.0001% of Al and Cu, and 0.0010% of each other element. C_1, C_2, and C_3 contain 0.00025% of Al and Cu and 0.0025% of each other element. D_1, D_2 and D_3 contain 0.0005% of Al and Cu and 0.0050% of each other element.

tivity for the lead determination in an air-acetylene flame is about 0.25 μg Pb/ml at 1 percent absorption. The detection limit is 0.1 μg Pb/ml.

b) Determination of Lead and Iron in Engine Combustion Chamber Deposits

These samples were thoroughly ground in a mortar prior to analysis to obtain uniform samples. The ground sample was dissolved in nitric acid and lead determined by atomic absorption. A portion of the sample solution was also used in the determination of iron. Iron is reduced with hydroxylamine to the ferrous state, and reacted with 1,10-phenanthroline in an acetate buffered solution (pH 5) to form an orange-red complex. Photometric measurements were made using a Beckman DU-2 spectrophotometer. Operating conditions were as follows: sensitivity setting - 2, slit opening - 0.10 mm, wavelength - 510 mm, 40 mm optical cells. The concentration of iron was determined from a standard curve. For a one gram sample diluted to 100 ml, the detection limit is about 1 ppm and the sensitivity ±1 ppm.

c) Gravimetric Method for Lead Determination in Millipore Filters

Following nitric acid digestion, concentrated sulfuric acid was added to the sample to precipitate lead sulfate. The solution was filtered, and the precipitate dried and weighed to determine the amount of lead percent. In addition, the filtrate was analyzed by atomic absorption for trace amounts of lead. This analysis is included in the total amount of lead reported for the sample.

d) Determination of Lead and Other Metals in Glass fiber Filters

The glass fiber filters cannot be digested completely with nitric acid. They were cooked with concentrated nitric acid for two hours to leach out the metals. The pulp was filtered and washed and the filtrate analyzed by atomic absorption for lead, and by emission spectroscopy for other metals.

3) Scanning Electron Microscopy (SEM) and X-ray Fluorescence

The Scanning Electron Microscope (SEM) was used to identify (X-ray spectrometer) the collected exhaust particles from the Andersen Sampler and the Millipore backup filter.

a) Instrumentation

Cambridge Stereoscan Mark 2A

Ortec Non-dispersive X-ray Detector

Nuclear Data Analyzer

Varian Vacuum Evaporator

Kinney Vacuum Evaporator

b) Work Outline

(1) Particle characterization (SEM) on plates of Andersen Sampler

(2) Particle identification (X-ray)

(3) Single element X-ray scan

(4) X-ray spectra on impingement area of Andersen plates and spectra on backup filter

c) Techniques and Methods

(1) Substrates for sample collection: The most satisfactory substrates for photomicrography were micro cover glasses, while where X-ray analysis was employed, ultra pure carbon strips proved best. Silica interference from micro cover glasses, halogens in epoxy, and thermal instability in mylar film reduced the desirability for using these materials as substrates where X-ray analysis was to be carried out.

(2) Storage and sample preparation: All samples were maintained in a dry atmosphere from collection to examination. Both the glass cover slip and the carbon strip substratum were attached to SEM sample stubs with conducting silver paint. Samples for SEM characterization were made conductive with a thin layer (~200 Å) of gold or gold-palladium evaporated. Graphite carbon was sputtered on the samples used for X-ray diffraction.

(3) Normal operation for the Stereoscan:

(a) Gun potential - 20 to 30 kV (depending on sample degradation and resolution needed).

(b) Vacuum - $\sim 10^{-4}$ Torr.

(c) Sample angle - 20°.

(d) Working distance - 11 mm.

(e) Polaroid P/N Type 55 film with 100 sec exposure.

(4) Normal operations for X-ray Spectrometer (warranted 215 ev FWHM resolution):

(a) Gun potential - 30 kV

(b) 1024 channel - Series 2100 Nuclear Data Multichannel Analyzer

(c) Collection time - 200 sec

(d) Count rate - ~60 c.p.s.

(e) Spectra recorded on Moseley 7035B X-Y Recorder

(f) Single channel recording

(g) Polaroid P/N Type 55 film 400 sec or 800 sec exposure depending on concentration

d) Analysis

(1) Particle characterization and photomicrographical documentation was done with the scanning electron microscope employing standard operational procedures.

(2) Particle identification involved elemental analysis using the X-ray spectrometer on the scanning electron microscope. This included, for multiple particles, full spectrum elemental scan, and single element scan. Spot scans were carried out on single particles or in specific regions of particles.

7. Condensate Analyses

Condensate was collected from the raw exhaust as described in Section III-C. The condensate was analyzed for aldehydes and NH_3 using the procedures outlined below.

a. Aldehydes

The analytical method for the determination of carbonyl compounds in automotive exhaust emissions employed polarographic techniques. Samples for analysis were collected from undiluted exhaust effluent using ice-water cooled cold traps and via a sample probe welded into the engine or vehicle exhaust system. A Princeton Applied Research Model 170 Electrochemistry System was used as the monitoring device. The derivative pulse polarographic mode yielded the best combination of carbonyl compounds. A dropping mercury electrode with a Princeton Model 172 Drop Timer was employed as the working electrode.

Hydrazine derivatives (hydrazones) were employed for the determination of the carbonyl compounds, since hydrazones are easier to reduce than the free compounds, thus eliminating many possible interferences.

An acetate buffer of approximately pH 4 (an equimolar mixture of acetic acid and sodium acetate, 0.1 M in water) was used to control pH for hydrazone formation and also acted as supporting electrolyte. Hydrazine was added as a 2 percent aqueous solution. In this system formaldehyde gave a peak potential (half-wave potential) of -0.92 v vs. a saturated calomel reference electrode. A platinum wire was employed as the auxiliary electrode.

With the above system, it is possible to distinguish between and simultaneously determine aromatic aldehydes, formaldehyde, higher aliphatic aldehydes, and aliphatic ketones as shown in Figure 5.

Since aromatic ketones, e.g. benzophenone, give polarographic response in pH 4 buffer without hydrazine, it is also possible to detect aromatic ketones. Lead and zinc could also be determined from the samples under these conditions.

Since formaldehyde was the main carbonyl component of the condensate samples, all results were calibrated against and reported as formaldehyde. The upper curve in Figure 6 shows an actual sample without hydrazine present and demonstrates the lack of interference in the carbonyl region. The lower curve shows the same sample after the addition of hydrazine. Figure 7 shows the same solution after the addition of a formaldehyde standard. These two figures clearly establish the presence of formaldehyde in the exhaust samples.

Procedure:

Pipet 2 ml of methanol sample into a 25-ml volumetric flask. Add 10 ml of pH 4 acetate buffer and dilute to volume with water. Transfer this solution to a polarographic cell and deaerate with oxygen-free nitrogen for ten minutes. Record a derivative pulse polarogram from 0 to -1.6 v vs. SCE. Add 2 ml of hydrazine reagent to the polarographic cell and deaerate for 5 minutes. Again, record the polarogram from 0 to 1.6 v vs. SCE.

Lead and aromatic ketones are determined from the waves obtained without hydrazine at the peak potentials listed above. Formaldehyde, higher aliphatic aldehydes, aromatic aldehydes, and aliphatic ketones can be determined from the second polarogram with hydrazine present.

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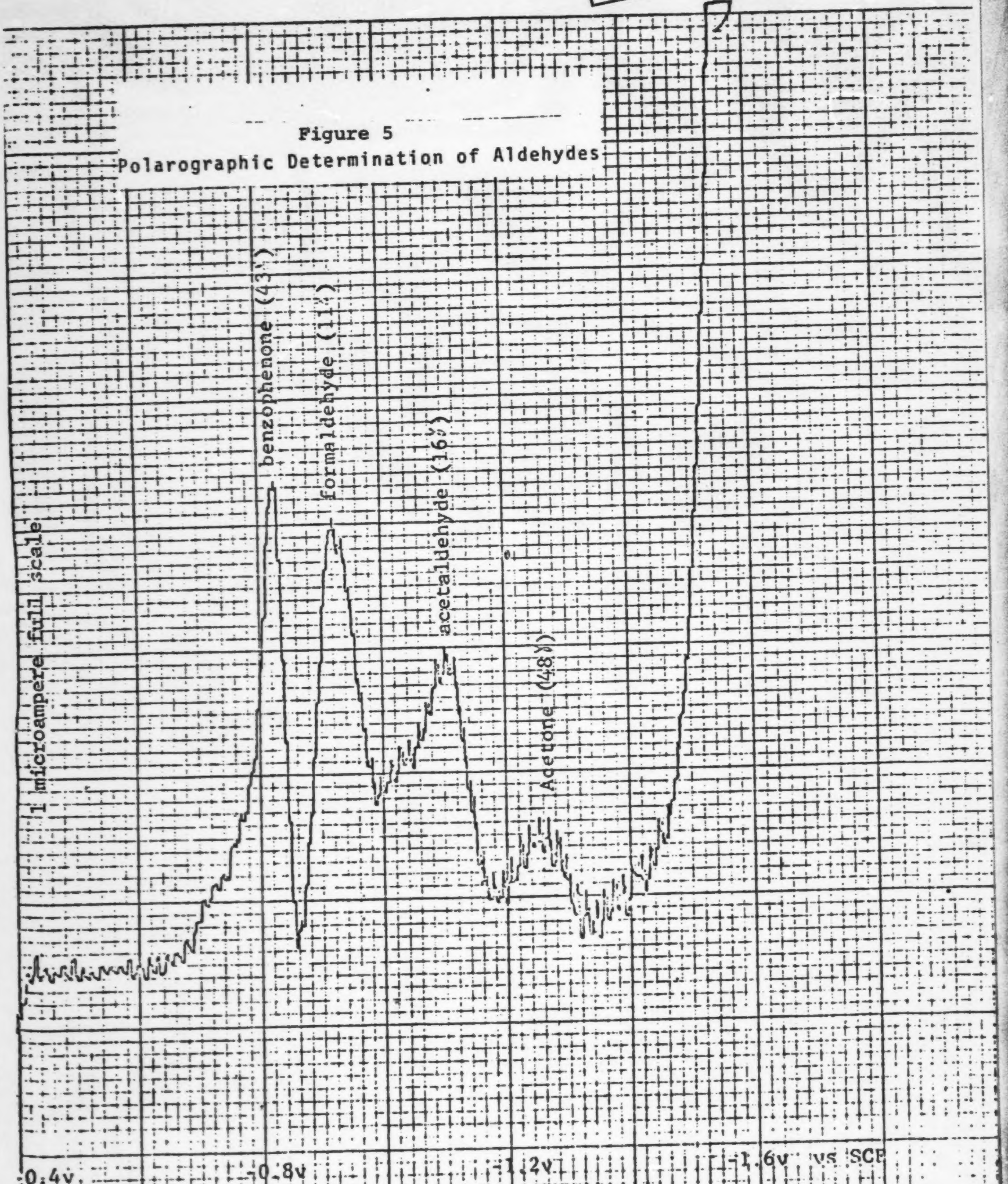
Figure 5
Polarographic Determination of Aldehydes



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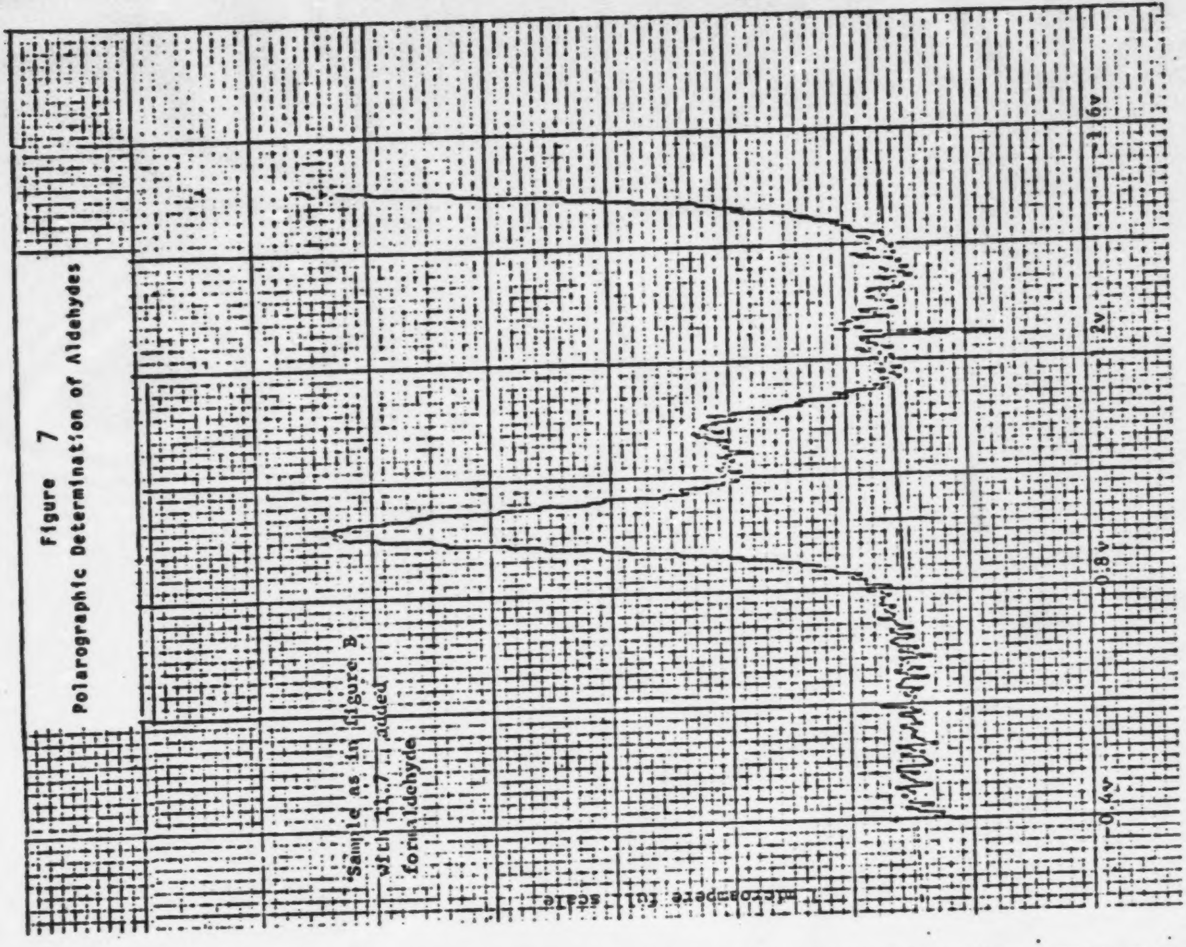


Figure 7
Polarographic Determination of Aldehydes

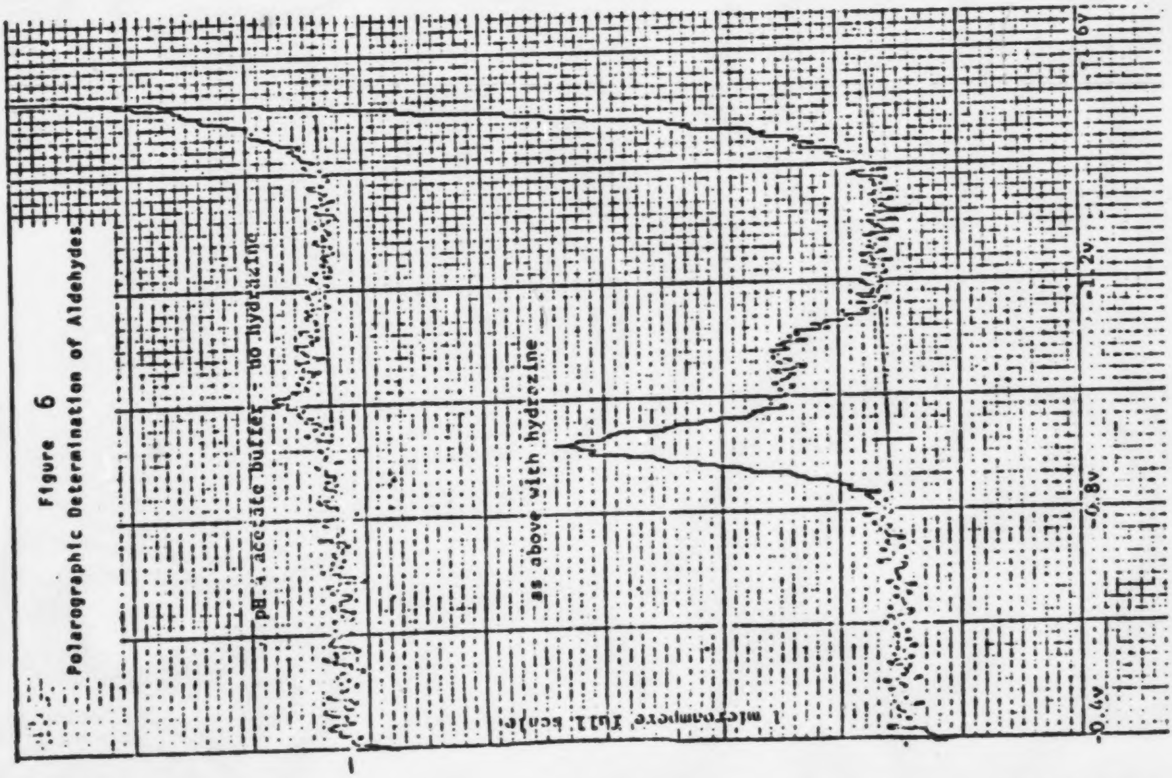


Figure 6
Polarographic Determination of Aldehydes

All responses should be calibrated by addition of known amounts of standard compounds to actual runs. Peak heights are linear with concentration.

In this system, zinc has a peak potential of -1.00 v vs. SCE, but it can be differentiated from benzophenone by the fact that it possesses only one polarographic wave.

A blind comparison of the polarographic technique vs. the MBTH technique was made, and the results were as follows, expressed as formaldehyde:

MBTH	Polarographic
340 ppm	300 ppm
1500 ppm	1530 ppm
430 ppm	480 ppm
105 ppm	110 ppm
150 ppm	110 ppm

b. Ammonia

Ammonia was present in the exhaust gas condensate and was analyzed in the following manner.

A 5-10 cc aliquot of condensate was added to a 50 percent potassium hydroxide solution. This mixture was then steam distilled into an excess of 0.010 N hydrochloric acid. The excess acid was determined by adding potassium iodide and iodate and titrating the liberated iodine with 0.010 N sodium thiosulfate.

This technique is capable of determining ammonia as low as 0.3 ppm. Figure 8 is a sketch of the apparatus used for the determination.

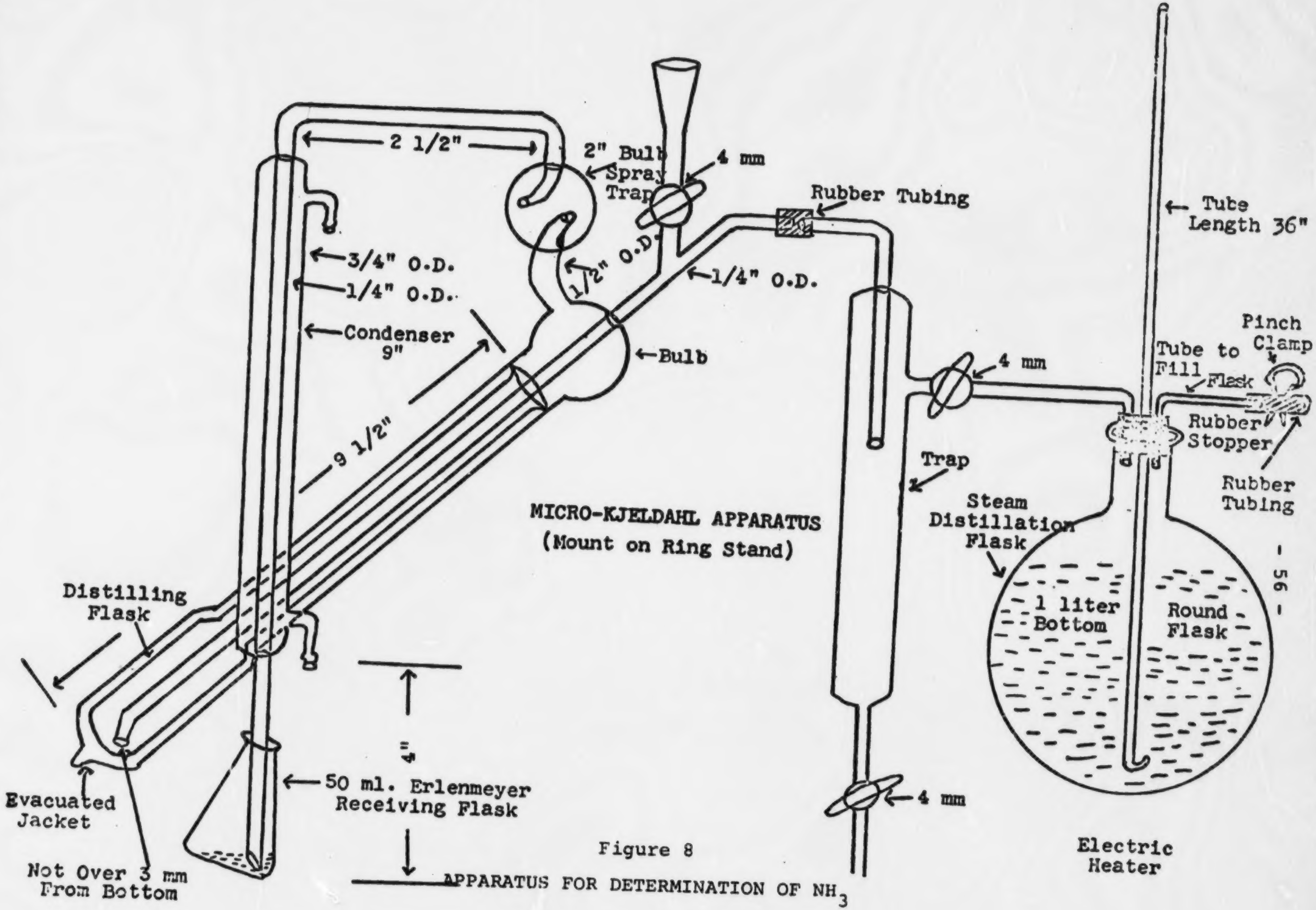

MICRO-KJELDAHL APPARATUS
(Mount on Ring Stand)
2 1/2"
2" Bulb Spray Trap
4 mm
Rubber Tubing
Tube Length 36"
3/4" O.D.
1/4" O.D.
1/2" O.D.
1/4" O.D.
Condenser 9"
Bulb
9 1/2"
4 mm
Pinch Clamp
Tube to Fill Flask
Rubber Stopper
Rubber Tubing
Trap
Steam Distillation Flask
1 liter Bottom
Round Flask
Distilling Flask
4"
50 ml. Erlenmeyer Receiving Flask
4 mm
Evacuated Jacket
Not Over 3 mm From Bottom
Electric Heater

Figure 8

APPARATUS FOR DETERMINATION OF NH_3

The analytical procedures given herein have been adapted from literature sources or developed upon the basis of experimental data which are believed to be reliable. In the hands of a qualified analyst they are expected to yield results of sufficient accuracy for their intended purposes. However, The Dow Chemical Company makes no representation or warranty whatsoever concerning the procedures or results to be obtained and assumes no liability in connection with their use. Users are cautioned to confirm the suitability of the methods by appropriate tests.

V. EXPERIMENTAL RESULTS

The primary goal of this contract was to develop a test procedure which would be reproducible, reasonable inexpensive, and which could be performed in other test facilities with a minimum of modifications to existing equipment, for the purpose of evaluating any negative or positive effectives of a given fuel additive on particulate exhaust emissions. Included in this section will be the data generated while trying to establish a consistent testing method. The basic method was generally described in Section III.

A. SPECIFIC CONCLUSIONS

1. Additive B, (an amine detergent) at the then manufacturer's recommended level, increased particulate emissions in both engine stand and vehicle test runs, from 50% to 100% above the baseline (Figures 9, 10, 15) when collected on the 142 mm glass fiber filters. Increases in particulate with the use of Additive B fuel were also noted in the Andersen separator and back-up filter, but the increases were not as pronounced.

2. Additive A (a manganese antiknock) at the manufacturer's recommended level, did not significantly increase or decrease the particulate emission levels in the vehicle test runs (Figures 9 through 12).

3. Additive A, at the manufacturer's recommended level, slightly decreased the particulate emissions under 23-minute Federal cycle cold start and hot start conditions, when tested on the engine stand (Figures 15, 16).

4. Additive B increased unburned hydrocarbons in the raw exhaust under both steady-state and 23-minute Federal cycle cold start conditions, when tested in the vehicles (Figures 13,14).

5. Additive A did not significantly increase or decrease unburned hydrocarbons under either steady-state or cyclic conditions when tested in the vehicles (Figures 13,14).

6. The use of Additive B, at three times the manufacturer's recommended level, gave particulate emission increases varying from 8 times greater than the baseline and 5 times greater than the particulate measured at the recommended dosage level, when tested under Federal cycle cold start conditions (Figures 15, 16) and collected on 142 mm glass filters. The respective increases for the Andersen plus back up filters are 3 times the baseline and 9 times the 1X concentration.

7. The use of Additive A at three times the manufacturer's recommended level gave no significant increase in particulate emissions compared to the baseline or to the recommended dosage level (Figures 15, 16).

8. Increasing the additive dosage to three times the manufacturer's recommended level caused the same general effect on particulate emissions after a 75-hour cyclic conditioning period on the engine stand, as was noted after approximately 17,000 miles of vehicle testing (Figures 9, 10, 15, 16).

9. The increase in particulate and hydrocarbon emissions noted with Additive B in the vehicle tests was a function of mileage and did not appear to level off until after 10,000 miles (Figures 9 through 14).

10. The particulate emissions measured after a 75-hour cyclic conditioning period on the engine stand using the manufacturer's recommended dosage correlates well with the measured particulate after 5,000 miles (break-in period plus 1,500 miles) of vehicle testing. A 75-hour sequence of 23-minute cycles equates to about 1,500 vehicle miles (Figures 9, 10, 15, 16).

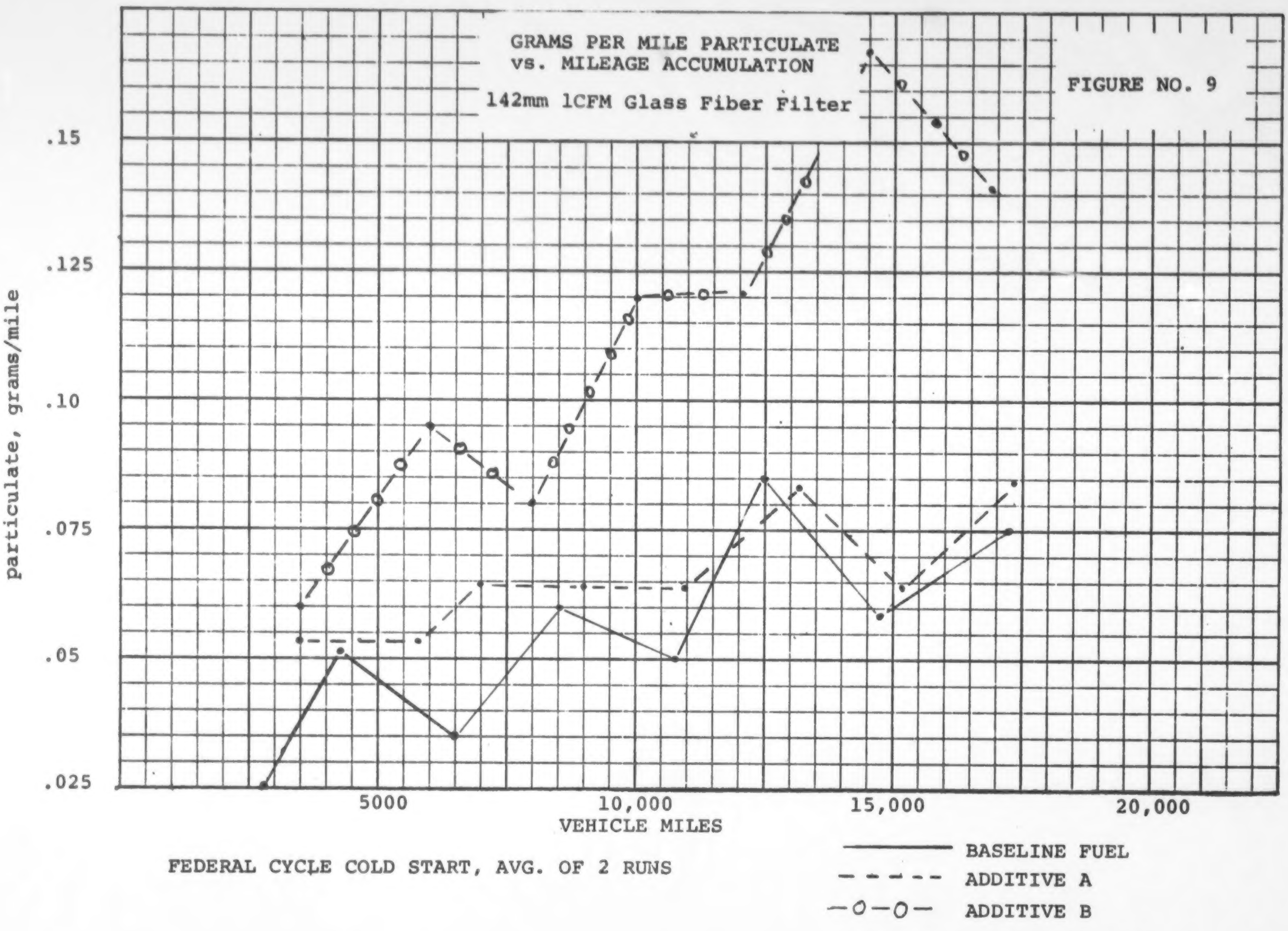


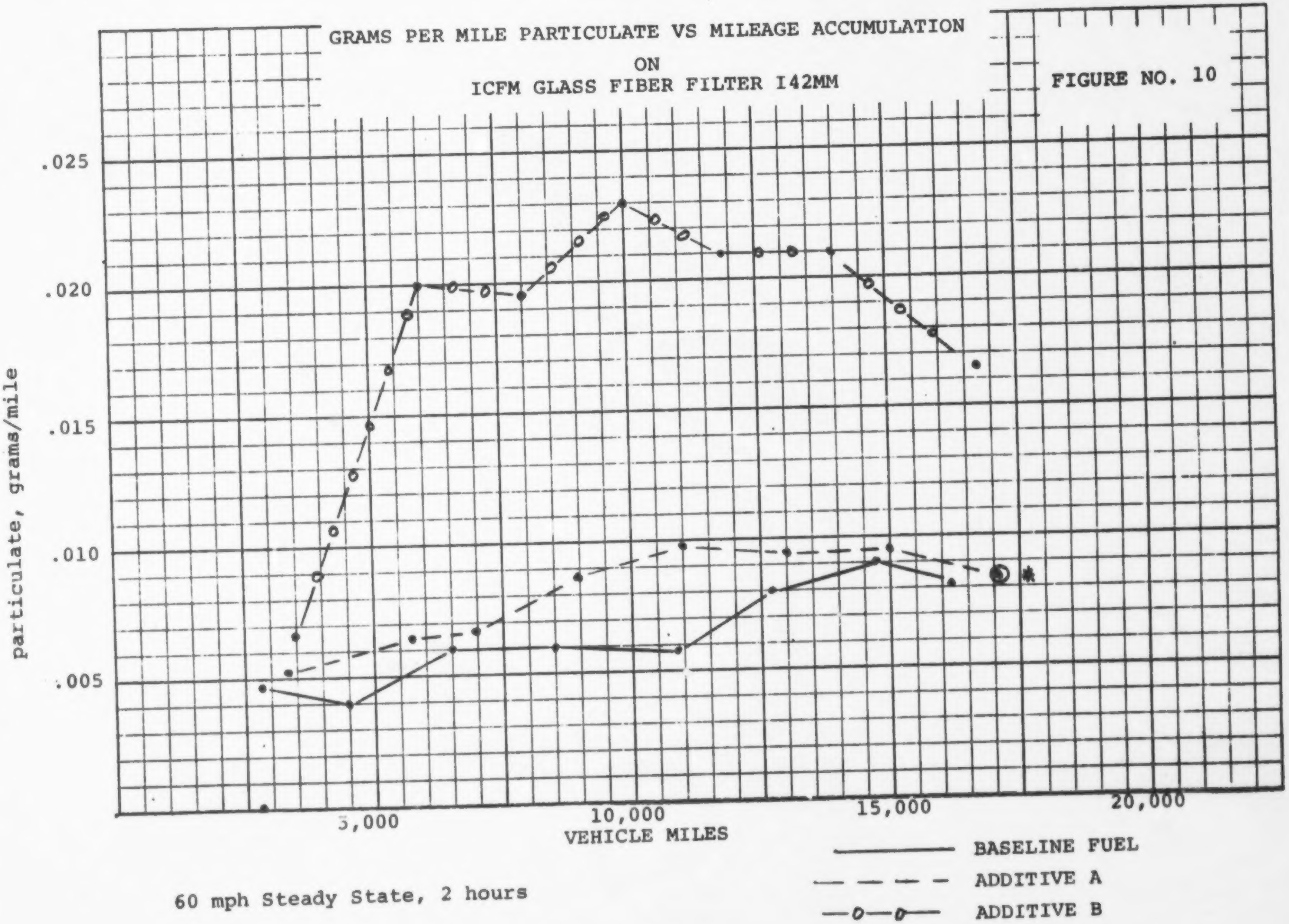
FIGURE NO. 9

GRAMS PER MILE PARTICULATE
vs. MILEAGE ACCUMULATION

142mm 1CFM Glass Fiber Filter

FEDERAL CYCLE COLD START, AVG. OF 2 RUNS

CHASSIS DYNOMOMETER



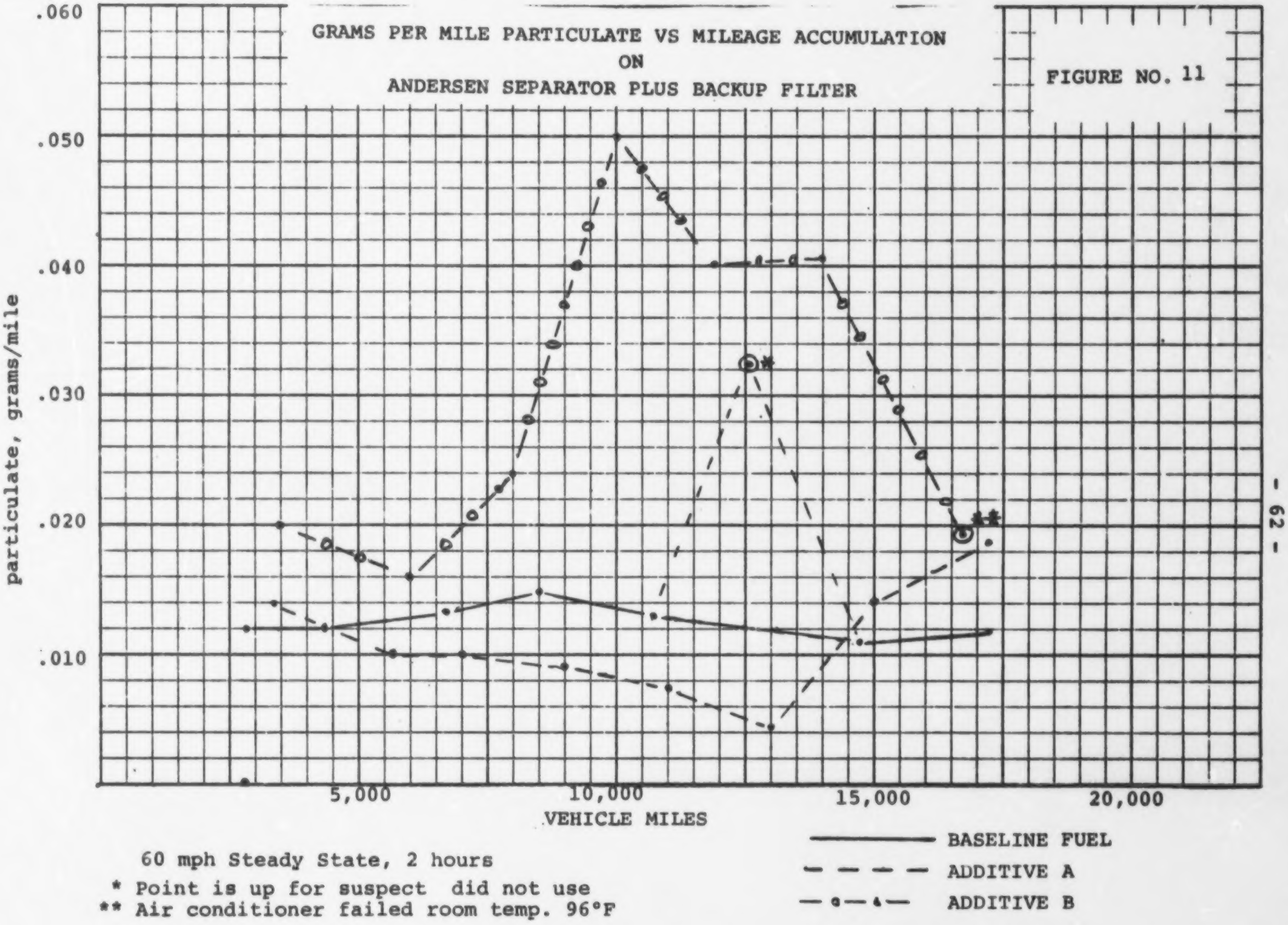
GRAMS PER MILE PARTICULATE VS MILEAGE ACCUMULATION
ON
ICFM GLASS FIBER FILTER I42MM

FIGURE NO. 10

60 mph Steady State, 2 hours

* Air conditioner failed room temp. 96°F

CHASSIS DYNOMOMETER



GRAMS PER MILE PARTICULATE VS MILEAGE ACCUMULATION
ON
ANDERSEN SEPARATOR PLUS BACKUP FILTER

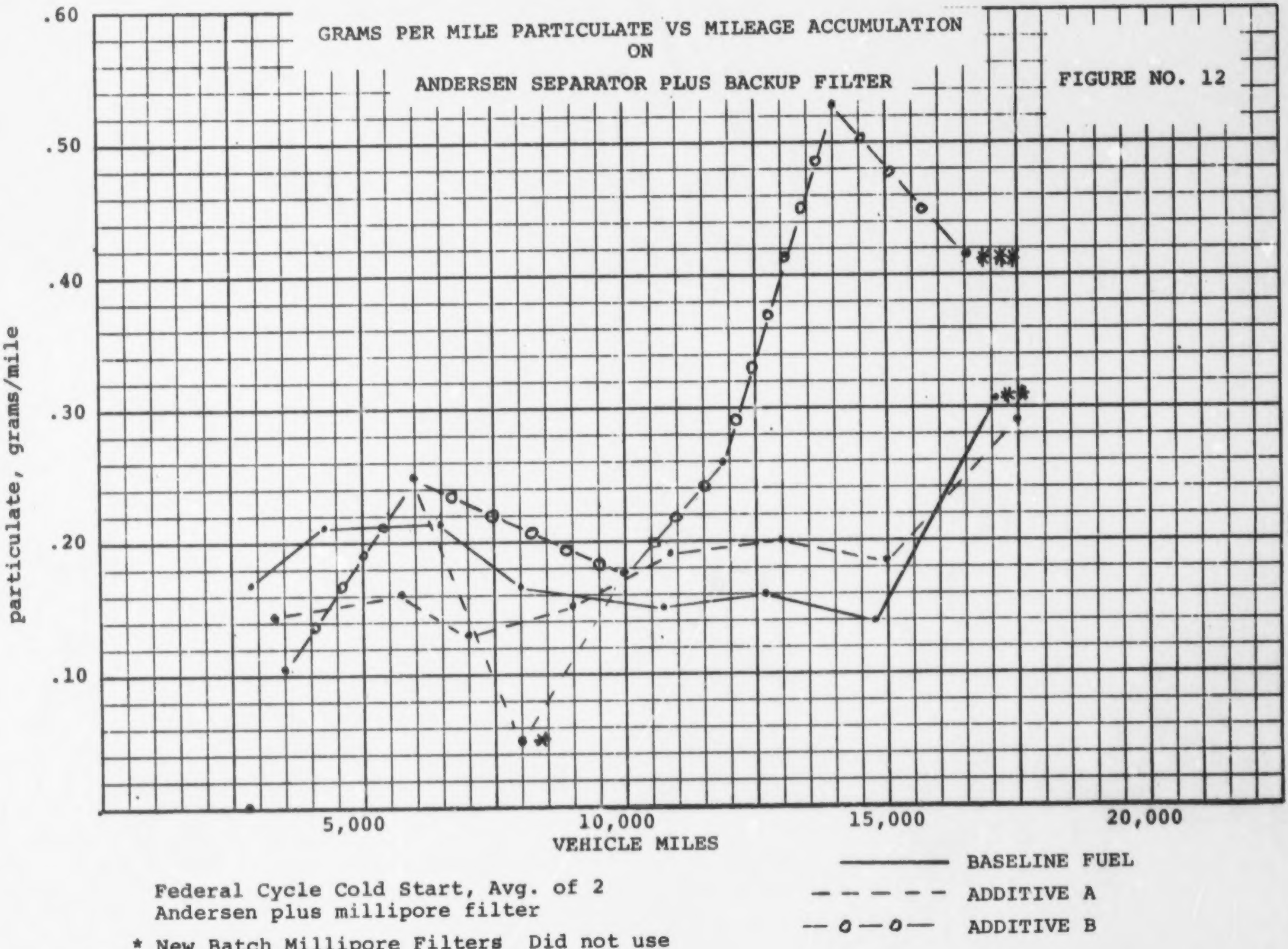
FIGURE NO. 11

60 mph Steady State, 2 hours

* Point is up for suspect did not use

** Air conditioner failed room temp. 96°F

CHASSIS DYNOMOMETER



GRAMS PER MILE PARTICULATE VS MILEAGE ACCUMULATION
ON
ANDERSEN SEPARATOR PLUS BACKUP FILTER

FIGURE NO. 12

Federal Cycle Cold Start, Avg. of 2
Andersen plus millipore filter

* New Batch Millipore Filters Did not use
** High Humidity Moisture On Filter
*** Air Conditioner broke down room temp. 96°F

CHASSIS DYNOMOMETER

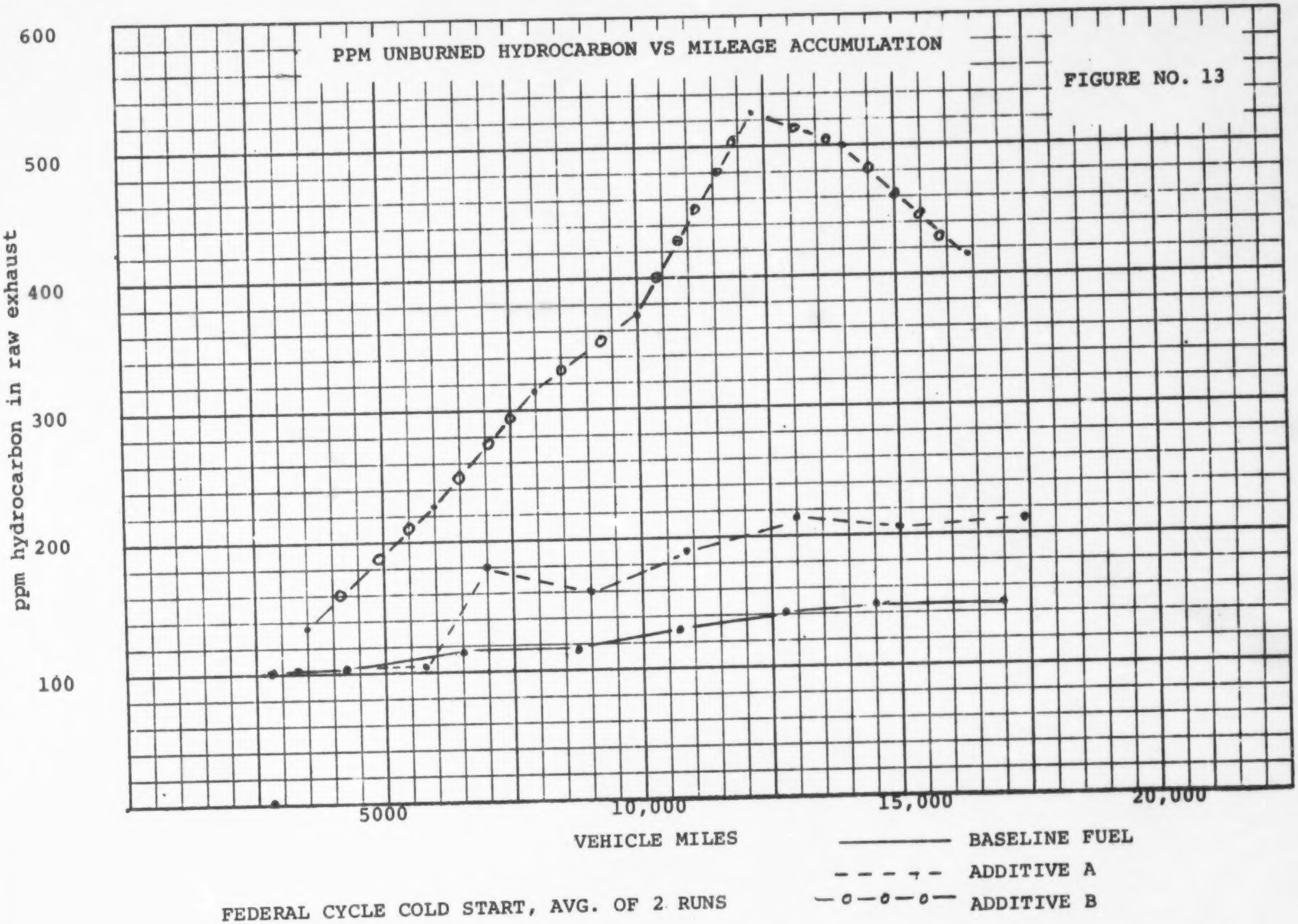


FIGURE NO. 13

PPM UNBURNED HYDROCARBON VS MILEAGE ACCUMULATION

FEDERAL CYCLE COLD START, AVG. OF 2 RUNS

CHASSIS DYNOMOMETER

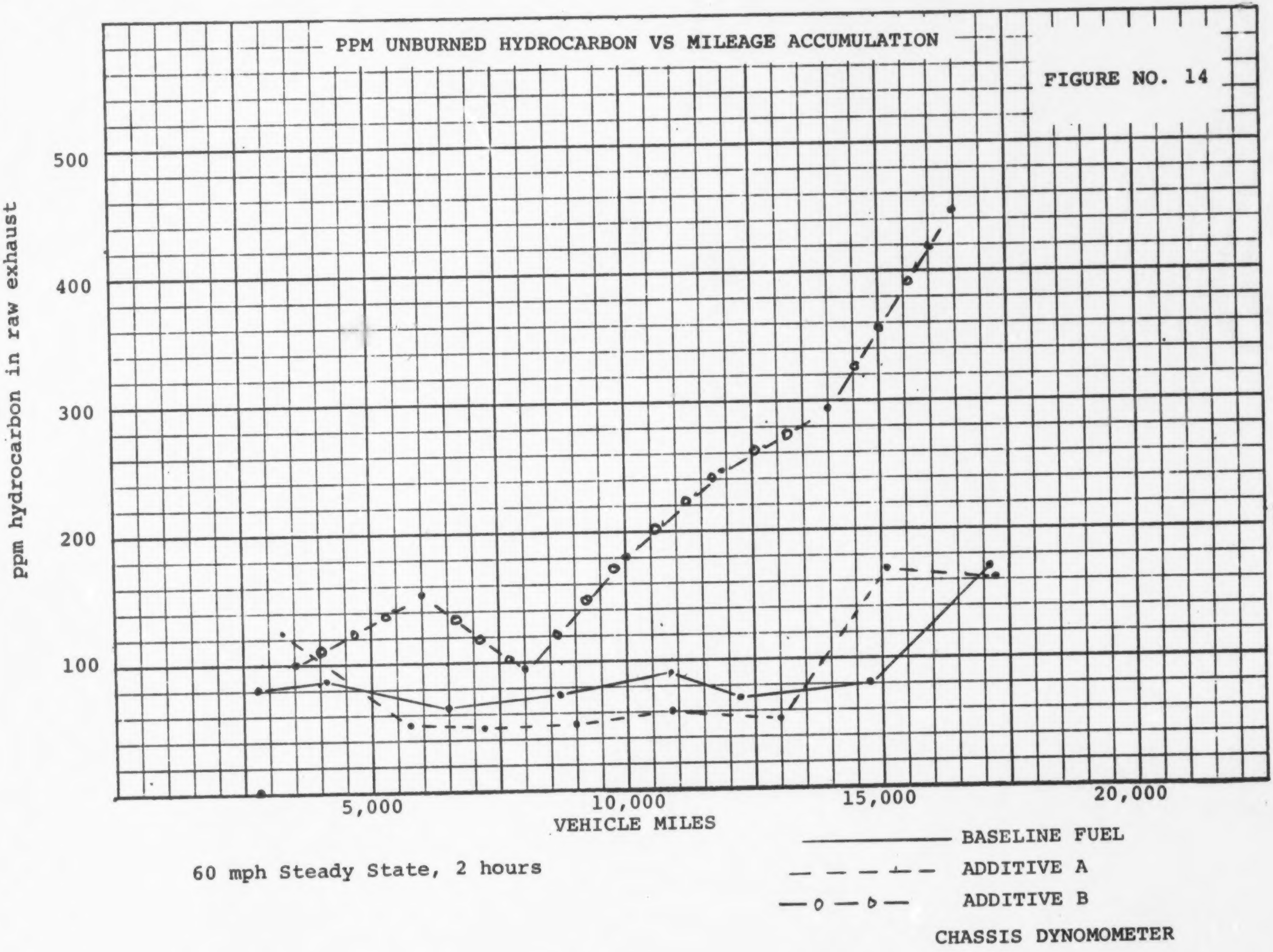


FIGURE NO. 14

PPM UNBURNED HYDROCARBON VS MILEAGE ACCUMULATION

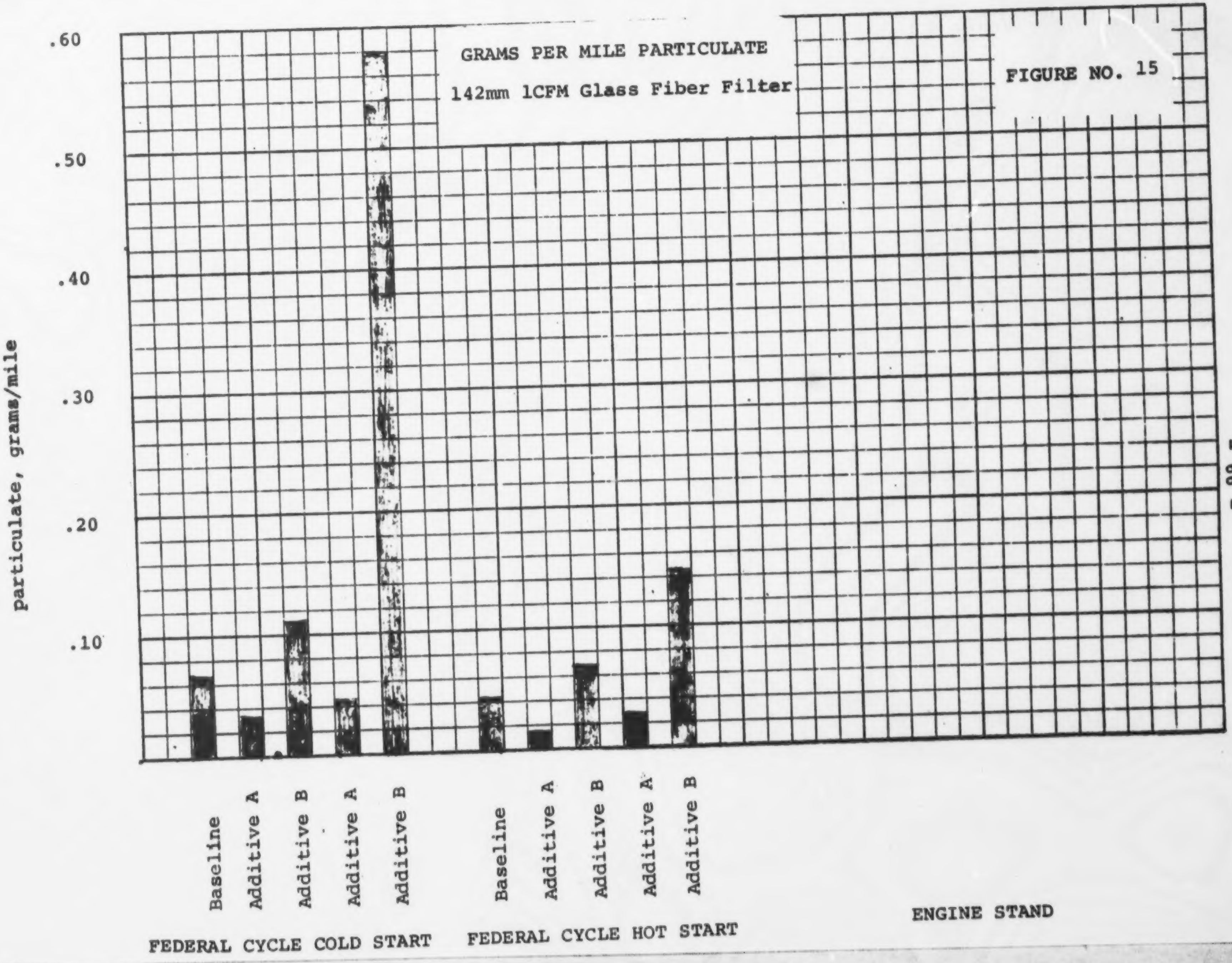
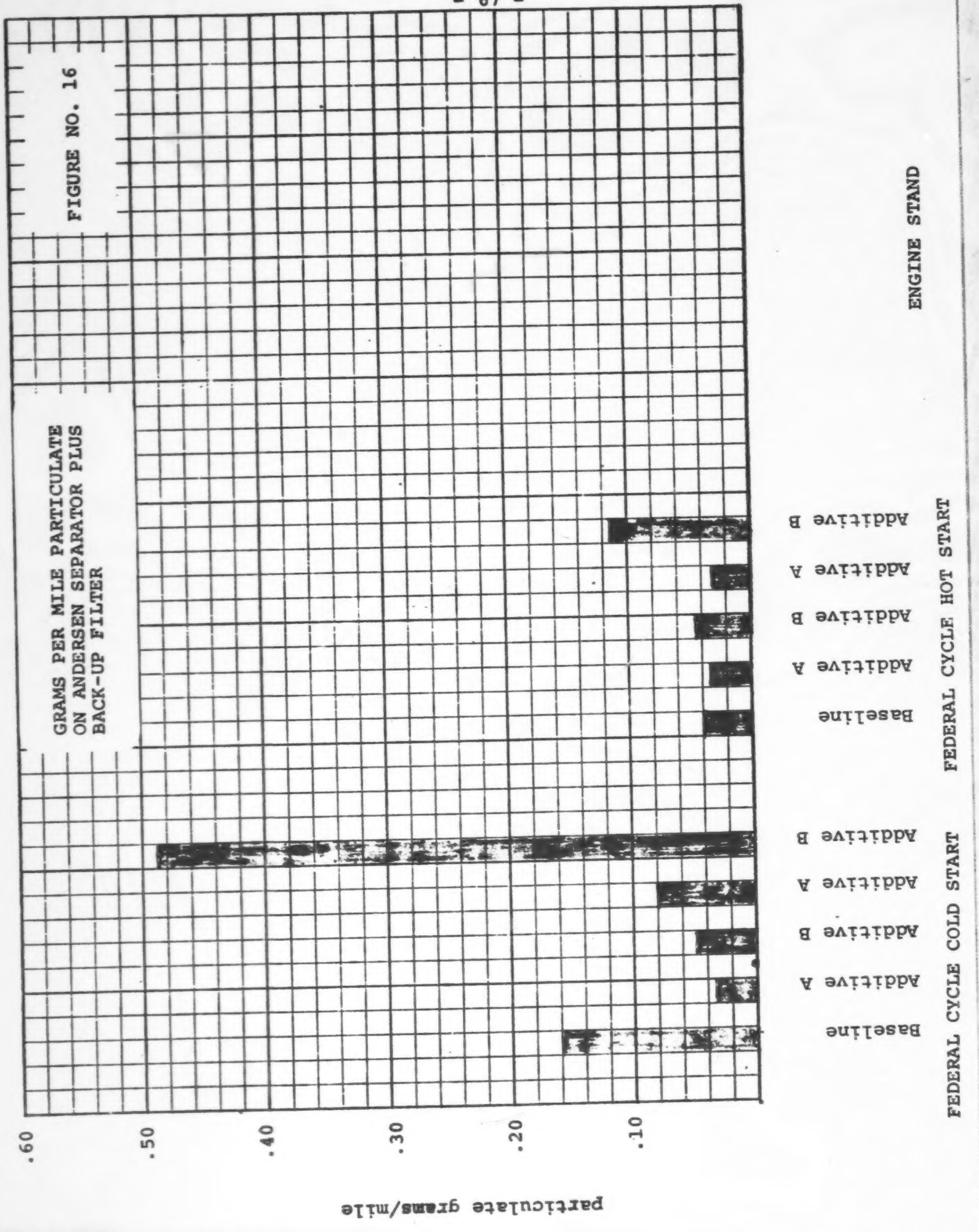


FIGURE NO. 15

GRAMS PER MILE PARTICULATE

142mm 1CFM Glass Fiber Filter

FIGURE NO. 16


GRAMS PER MILE PARTICULATE
ON ANDERSEN SEPARATOR PLUS
BACK-UP FILTER
particulate grams/mile
.60
.50
.40
.30
.20
.10
Baseline
Additive A
Additive B
Additive A
Additive B
FEDERAL CYCLE COLD START
Baseline
Additive A
Additive B
Additive A
Additive B
FEDERAL CYCLE HOT START
ENGINE STAND

11. Examination of the particulate by the scanning electron microscope showed differences in size distribution and particle shape between the baseline and the two additives tested.

B. FUEL AND ADDITIVES

The fuel used in all of the tests was Indolene O, to which the additives were added in the desired amounts. Table 9 is a listing of the pertinent physical and chemical data on the base stock fuel, as well as the physical and chemical analyses of the fuel after the additives were blended.

The additives which were used as references for the development of the methodology are described in Table 9. Both additives were blended into the fuel in two different concentrations. Additive A was used at 1.87 grams/gal., which was the level recommended by the manufacturer, and at 3 times the recommended level, or 5.61 grams/gal. Additive B was used at .9988 grams/gal., which is equivalent to .25 grams/gal. of manganese. At the time of the tests, this was also the level recommended by the manufacturer. The recommended usage rate has since been reduced. Engine runs were also made with 3 times the recommended level, or .75 g/gal. of manganese.

The vehicle tests were carried out using only the recommended levels of additives, while engine dynamometer studies were carried out with both concentrations.

C. TEST PROCEDURES

1. Engine Dynamometer

The engine was broken in according to the procedures outlined in Section III-A 1. After break-in, the engine was run 19

TABLE 9
GASOLINE ANALYSES

	Baseline	Additive A	Additive B	ppm Trace Metals	Baseline	A	B
Gravity	- 62.3	59.6	59.7	Fe	<1	7	1
1 BP	- 96	94	90	Ni	<1	1	<1
5%	- 118	124	122	Cu	.4	<.2	.3
10%	- 129	138	136	Al	<1	<1	<1
20%	- 148	157	163	Ca	<1	<1	<1
30%	- 168	179	179	Mg	<3	<3	<3
40%	- 192	200	198	Mn	<1	<1	61
50%	- 206	218	218	Pb	<3	<3	<3
60%	- 228	238	238	Cr	<1	1	<1
70%	- 246	252	258	Sn	<2	<2	<2
80%	- 270	278	284	Zn	<3	<3	<3
90%	- 311	312	326	Ti	<1	<1	1
95%	- -34	342	360	%C	85.9	86.0	85.9
EP	- 372	395	392	%H	14.0	13.6	13.6
RON	- 90.6	90.8	91.8	%S	.046	.047	.048
MON	- 80.4	80.2	81.5	ppm P	<.05	.20	.11
RVP	- 8.5	8.4	8.0				

NOTE: "Less than" means that none of the material in question was detected, and denotes the lower level of sensitivity for atomic absorption under the conditions of the analyses.

hours a day, with a 5-hour shut-down period, until approximately 75 hours had been accumulated. At the start of each 19-hour segment a gaseous exhaust analysis was run to determine the point at which the engine stabilized. Based on prior particulate loads, it was felt that in all cases, full stabilization was reached prior to 75 hours.

The 75-hour runs consisted of repeated 23-minute Federal cycles. These cycles were controlled by the mode monitor system described in Section III-A 1. At the end of 75 hours, particulate measurements were made using a single 23-minute Federal cycle. Both cold starts (12-hour room temperature soak period) and hot starts were run for particulate collection. The procedures used for collection and analyses are described in Section III-B, C, and D.

The engine tests were run in the following sequence:

1. Additive A at 1.87 g/gal. See Table 10.

2. Additive A at 5.61 g/gal.

3. The engine was then disassembled, deposits were cleaned out, new exhaust was installed.

4. Additive B at .25 g/gal. of manganese. The engine was again dissambled, deposits were removed, and new exhaust system installed.

5. Baseline fuel, with no additives. Engine disassembled, deposits cleaned, and new exhaust installed.

6. Additive B .75 g/gal. of manganese

TABLE 10
FUEL ADDITIVES

	Name		Use Level gm/gal	
Code	Chemical	Function	1x	3x
A	Polybuteneamine	Deposit Modifier	1.87	5.61
B	Methylcyclopentadienyl Manganesetricarbonyl	Octane Improver	0.25	0.75

It was felt that the baseline run would be more meaningful if it were run at some point in the middle of the tests, rather than at the beginning, since any changes in the engine due to the use of the additive at 3 times the concentration would be noted. The use of additive A at recommended levels was not expected to have any negative effects on the engine, while the 3x effect was unknown. Additive B, containing an inorganic functional group, was expected to give more engine deposits, and therefore the 3x concentration was run last.

2. Vehicle Tests

Three 1972 Chevrolets, equipped with an automatic transmission, air conditioning, and a 350 CID engine, were used for mileage accumulation studies for each additive and a baseline. The additive concentrations used in the vehicle fuels were at the manufacturer's recommended level, or .25 g/gal. of manganese for Additive B and 1.87 g/gal. of Additive B. All of the vehicles were operated on baseline fuel for 2,000 miles, after which the two additive cars were switched to their respective fuels.

Blowby tests (Section III-A) were run every 1,000 miles until it was determined that the engine had stablilized. Figures 17,18, 19 show the measured blowby at three different points in each vehicle's life. It is apparent that all three vehicles stabilized relatively quickly, with no abnormalities showing up in the blowby results.

The vehicles were driven by Dow employees in normal driving situations. Some care was exercised in ascertaining that the vehicles were not driven for prolonged periods of time above 70 mph, the maximum posted speed limit on Michigan highways. The vehicles were periodically rotated between drivers so that each vehicle had a somewhat similar operating history.

Figure 17

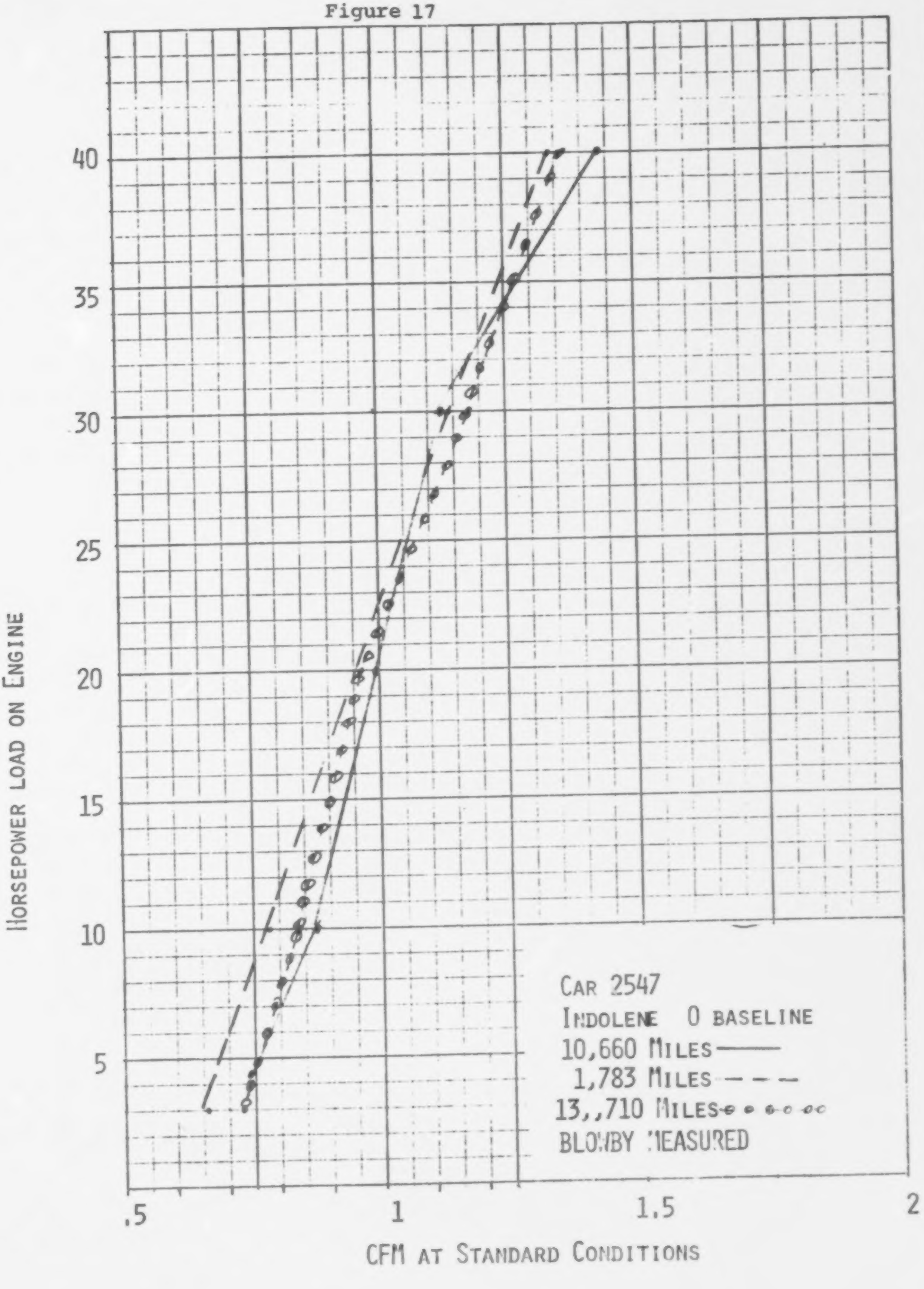

40
35
30
25
20
15
10
5
.5
1
1.5
2
Horsepower Load on Engine
CFM at Standard Conditions
Car 2547
Indolene 0 baseline
10,660 Miles ———
1,783 Miles – – –
13,,710 Miles ⊘ ⊘ ⊘ ⊘ ⊘
Blowby Measured

Figure 18

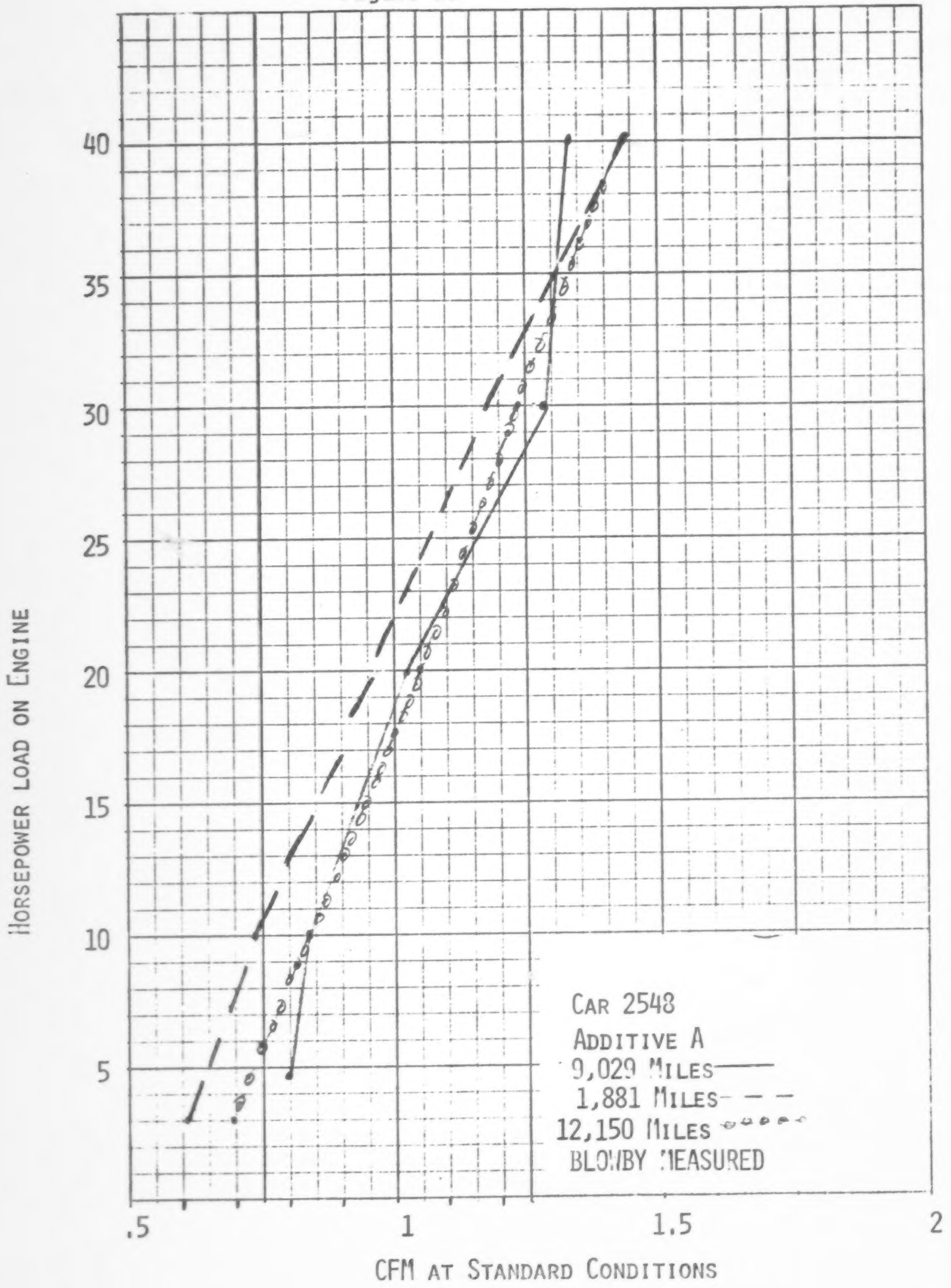
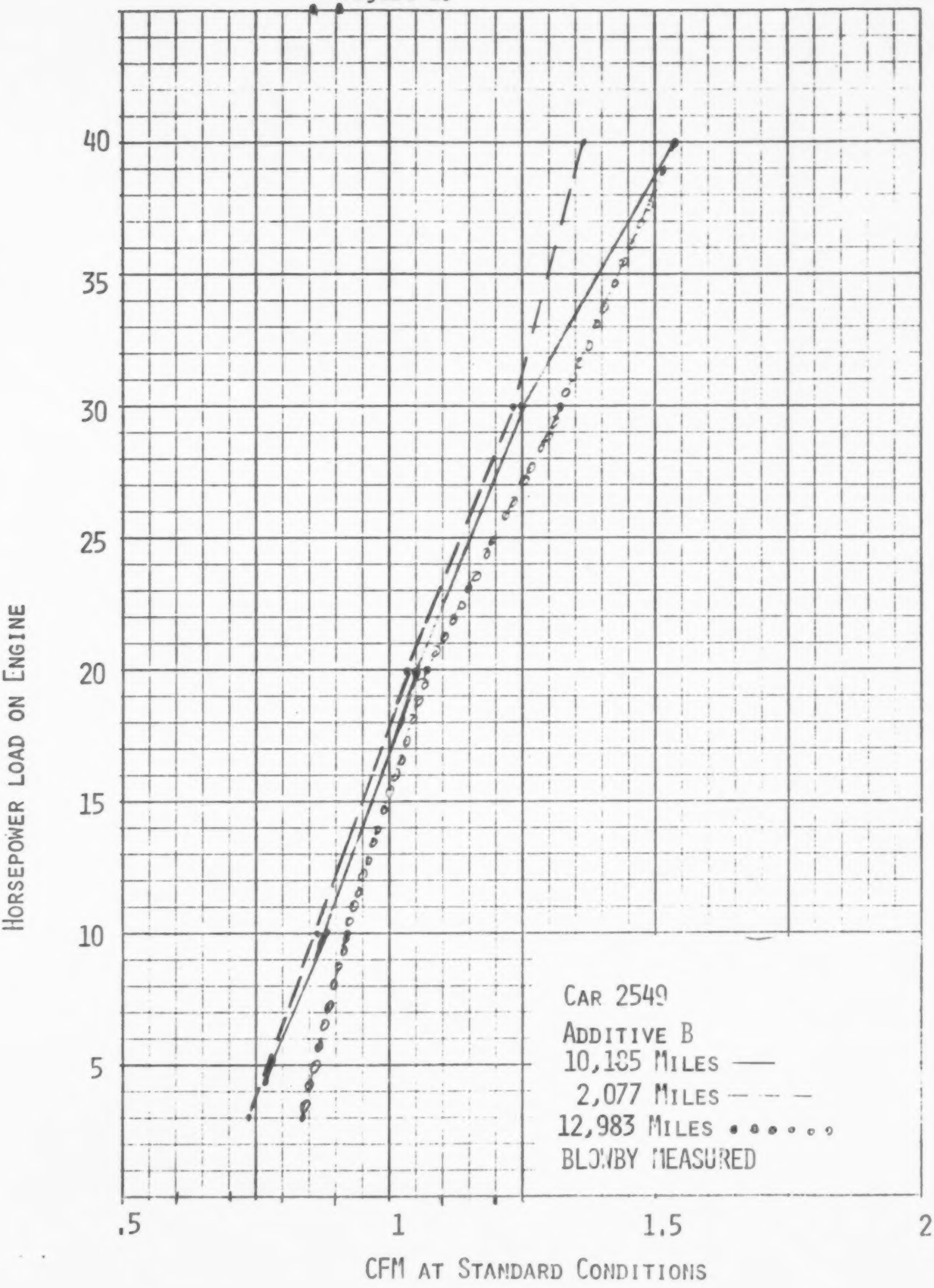

Horsepower Load on Engine
40
35
30
25
20
15
10
5
.5
1
1.5
2
CFM at Standard Conditions
Car 2548
Additive A
9,029 Miles
1,881 Miles
12,150 Miles
Blowby Measured

Figure 19


40
35
30
25
20
15
10
5
.5
1
1.5
2
Horsepower Load on Engine
CFM at Standard Conditions
Car 2549
Additive B
10,185 Miles ——
2,077 Miles — — —
12,983 Miles • • • ○ ○ ○
Blowby Measured

D. DATA

Tables 11, 12, 13 are a compilation of the data generated during the 75-hour engine runs. The particulate measurements and analyses were made on individual 23-minute Federal cycles at the conclusion of the 75-hour conditioning. Tables 14, 14, and 16 are compilations of the data generated over the lifetime of the vehicles under test.

E. DISCUSSION OF RESULTS

The primary purpose of this contract was to develop an engine stand method which would determine any effect of a given additive on the particulate phenomena noted in a vehicle operating on fuel using that additive. The purpose was not to determine whether the two additives under test were good or bad. Any conclusions drawn from the data presented herein are done so solely for the purpose of validating the proposed method.

1. Vehicle Particulate Emissions

By approximately 17,000 miles, the vehicles began to show a definite pattern as to the grams/mile emission measured from each one. Figures 9 and 10 (pg. 60 & 61) show graphically the particulate emission rate as a function of miles. Additive B appeared to cause a substantial increase in particulate emissions, while Additive A caused neither an increase nor decrease compared to the baseline. The 142 mm, 1 cfm filter gave the most consistant results, while the Andersen impactor plus Millipore (Figures 11 and 12) gave more scatter (pg. 62 & 63).

2. Engine Stand Particulate Emissions

The particulate emissions measured at the conclusion of the 75-hour conditioning sequence are shown graphically in Figures 15 and 16 (pg. 66 & 67).

The 23-minute Federal cycle is equivalent to about 7.5 miles of driving. Therefore, 75 hours of continuous 23-minute cycles represent only about 1,500 miles of vehicle operation. The particulate emission increases noted using Additive B at recommended levels in the vehicles showed up to a lesser degree in the engine runs, as was to be expected. However, when the additive concentration was tripled, the increased particulate which showed up with Additive B in the vehicle tests was duplicated in the engine runs, while the particulate levels of Additive A were not significantly different from the baseline.

3. Particulate Composition

The particulate emissions generated under both the engine and vehicle test programs were analyzed for trace metals, C, H, N, Benzo-α-pyrene, and benzene solubles. This data is included in Tables 11 through 16. Some significant conclusions from the analyses are as follows:

a. As might be expected, the manganese containing Additive B gave particulate high in manganese. Additive B showed a lower percentage of C, H, and N in the particulate, and in general, lower benzene solubles, than the baseline or the Additive A. However, in total there appeared to be more organic particulate present using Additive B since the total mass was larger.

b. Additive A showed higher Benzo-α-pyrene in the particulate from the engine runs and from the engine deposits taken from the vehicles, while the exhaust particulate Benzo-α-pyrene compared to the baseline vehicle run was inconclusive. Additive B showed lower ppm of Benzo-α-pyrene, as would be expected since the total mass was larger.

c. In general, the analyses for C, H, and N showed wide variations. It is difficult to make any meaningful conclusion, per se, since the precision of the technique used is so dependent on sample size, and since the sample sizes in general were so small.

d. The carbon content of the particulate collected from the 60 mph steady state vehicle runs decreased from 36% to 8% for the baseline fuel over the 17,000 mile test period, while remaining virtually constant at around 20% for Additive B over the same mileage. Additive A showed an initial increase from 40% to 78% carbon, with a subsequent decrease to 25%. Although the carbon content decreased for the baseline, the total particulate mass emissions under these conditions remained relatively constant. The Additive B mass emissions increased, while the carbon content remained constant.

e. The correlation between the engine runs and the vehicle tests with respect to C, H, and N analyses of the particulate is not good. The most important factor contributing to this is the small sample size collected under the Federal Cycle. The steady state collection on the vehicles gave enough sample for relatively precise analyses, but the 23 minute cycle generally produced such small amounts of collected particulate that analytical precision was low. No steady state collections were made on the engine runs.

TABLE 11

ENGINE DYNAMOMETER TEST

ENGINE TYPE: 1972 Chevrolet 350 CID

FUEL: Indolene # 15214

Additive		Conditioning Hours	Test Mode	Grams per Mile Particulate					Run No.
Type	Conc.			Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter 1 cfm	Glass Filter 47 mm	
Baseline	none	75	FCCS	.1246	.0293	.1539	.0696	.0146	240A
"	none	75	FCHS	.0268	.0146	.0414	.0440	.0146	240C

TABLE 11 Con't.

EXHAUST GAS ANALYSIS

	% by Volume				Parts per Million				Exhaust Condensate		
Run #	CO_2	O_2	N_2	CO	H.C.	NO_2	NO	NO_x-N_x	PPM HCHO	PPM NH_3	PPM HCHO in exhaust
240 A	13.0	1.5	84.0	.59	200		1100	297			
240 C	12.9	1.8	84.1	.38	170		1090	332			

TABLE 11 Con't.

ANALYSIS OF EXHAUST PARTICULATE

% on Millipore Filter

Run #	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	%C	%H	%N	benzene solubles	PPM BAP
240A	40	1.0	<2.5	5	4.5	2.0	<.2	1.0	--	<.5	2.0	.5	54.21	6.28	2.86	--	--
240C	33	1.5	< .4	3.2	8.3	0.5	<.2	0.7	--	<.4	.08	.08	40.1	5.16	0.58	51	28
Engine Deposits																	
Head	.6	<.005	.01	.07	.3	.4	.5	<.001	--	.5	<.005	2.0					
Piston top	.4	<.005	.5	1.5	.8	1.5	.3	<.001	--	1.3	<.005	2.0					
I. Valve	.6	.005	.03	.07	1.0	2.0	.3	.07	--	1.0	<.005	1.0					
Used Engine Oil	.8	<.002	.05	.07	4	6	<.2	.07	--	.2	.005	.4					
Unused Engine Oil	.0003	<.0001	.00006	.0001	.0011	1.36	.0001	.001	.0001	2.43	.0001	.0006					

TABLE 12

ENGINE DYNAMOMETER TEST

ENGINE TYPE: 1972 Chevrolet 350 CID

FUEL: Indolene # 15214 plus Additive A

Additive		Conditioning Hours	Test Mode	Grams per Mile Particulate					Run No.
Type	Conc.			Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter		
							1 cfm	47 mm	
A	1.X	75	FCCS	.0374	Nill	.0374	.0322	--	234 A
"	1.X	75	FCHS	.0244	Nill	.0244	.0070	--	234 B
"	1.X	75	FCHS	.0300	.0132	.0432	.0282	--	234 C
A	3.X	75	FCCS	.0586	.0220	.0806	.0464	.0366	238 A
"	3.X	75	FCHS	.0171	.0122	.0293	.0268	.0122	238 B
"	3.X	75	FCHS	.0171	.0171	.0342	.0353	.0146	238 C

TABLE 12 Con't.
EXHAUST GAS ANALYSIS

	% by Volume				Parts per Million				Exhaust Condensate		
Run #	CO_2	O_2	N_2	CO	H.C.	NO_2	NO	NO_x-N_x	PPM HCHO	PPM NH_3	PPM HCHO in exhaust
234A	13.1	2.0	83.8	.15	155				408		
234B	--	--	--	--	--				267		
234C	12.7	2.0	84.3	.03	190				127		
238A	12.3	2.8	83.7	.21	160				237		
238B	--	--	--	--	--				185		
238C	--	--	--	--	--				165		

TABLE 12 Con't.

ANALYSIS OF EXHAUST PARTICULATE

% on Millipore Filter

Run #	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	%C	%H	%N	benzene solubles	PPM BAP
234A	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--		--
234B	13.0	.09	<.5	4.6	8.1	.5	<.2	.02	--	<.5	.04	0.1	16.8	0.66	0.92		--
234C	5.6	.2	<.5	1.8	7.4	.9	.4	.4	--	<.5	.05	0.2	38.48	7.25	5.70		--
238A	3.7	.26	.24	1.1	15.9	4.3	.18	.40	.28	2.5	.22		37.08	2.95	.01	30%	700
238B	--	--	--	--	--	--	--	--	--	--	--		--	--	--	67%	100
238C	1.4	<.1	.93	.4	6.9	1.5	.05	.17	<.1	.8	.08		43.3	4.84	1.59	61%	480
Engine Deposits																	
Head	1.2	.009	.058	.05	.18	.2	.013	.01	.008	.003	.02	.9					
Piston top	.6	.007	.2	.2	.22	.3	.008	.01	.03	.5	.02	.8					
I. Valve	.09	.002	.015	.007	.02	.01	.001	.007	.001	.065	.003	.1					
Used Engine Oil	.02	.0001	.002	.0018	.06	.1	.0008	.001	.001	.10	.0001	01					
Unused Engine Oil	.0003	<.0001	.00001	.0001	.0011	1.36	.0001	.0001	.0001	2.43	.0001	.0006					

TABLE 13

ENGINE DYNAMOMETER TEST

ENGINE TYPE: 1972 Chevrolet 350 CID

FUEL: Indolene # 15214 plus additive B

Additive		Conditioning Hours	Test Mode	Grams per Mile Particulate					Run No.
Type	Conc.			Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter 1 cfm	Glass Filter 47 mm	
B	1.X	75	FCCS	.0440	.0073	.0513	.1100	.0440	239 A
"	1.X	75	FCHS	.0195	.0293	.0488	.0696	.0366	239 B
"	1.X	75	FCHS	.0171	.0244	.0415	.0708	.0366	239 C
B	3.X	75	FCCS	.3740	.1246	.4986	.5433	.5280	241 A
"	3.X	75	FCHS	.0464	.0757	.1221	.1588	.1197	241 B
"	3.X	75	FCHS	.0366	.0733	.1091	.1344	.0944	241 C

TABLE 13 Con't.
EXHAUST GAS ANALYSIS

Run #	% by Volume				Parts per Million				Exhaust Condensate		
	CO_2	O_2	N_2	CO	H.C.	NO_2	NO	NO_x-N_x	PPM HCHO	PPM NH_3	PPM HCHO in exhaust
239A	12.7	1.7	83.7	.81	390			1040	497		
239B	12.9	2.0	83.8	.43	340			1108	422		
239C	13.0	2.0	83.7	.38	345			1040	--		
241A	12.8	1.9	83.8	.60	520			1224	940		
241B	12.7	2.2	83.9	.35	465			1138	927		
241C	12.9	2.0	84.2	.03	475			1180	1061		

TABLE 13 Con't.

ANALYSIS OF EXHAUST PARTICULATE

% on Millipore Filter

Run #	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	%C	%H	%N	benzene solubles	PPM BAP
239A	8.7	.15	1.7	1.4	17.7	3.3	20.2	.35	.16	1.5	.3		29.1	1.1	.63	25.%	83
239B	1.2	.11	.59	.41	3.5	.98	34.1	.09	.11	.7	.07		28.0	3.26	.36	23.%	53
239C	--	--	--	--	--	--	--	--	--	--	--		--	--	--	30.%	30
241A	1.0	.06	<.1	1.0	2.9	.2	.7	.1	--	.1	.02	.5	13.9	1.22	1.57	5.2	72
241B	3.2	.1	<.08	1.3	2.1	.1	3.2	.1	--	.08	.01	.5	16.4	1.3	1.07	10.4	28
241C	1.6	.07	<.08	0.3	1.3	.1	3.3	.03	--	.08	.01	.4	18.9	1.75	1.03	9.2	<11
Dil. Tube **Sweepings**	2.0	.01	.03	.2	.15	1.2	10.0	.05	--	1.5	.005	.2					
Engine **Deposits**																	
Head	.6	.005	.01	.05	.4	.4	10	.001	--	.5	.005	2					
Piston top	.01	.005	.02	.2	.4	.5	1.5	.001	--	.5	.005	2					
I. Valve	.5	.02	.03	.04	.4	1.5	7.0	.05	--	.6	.005	.09					
Used **Engine Oil**	.7	.0004	.02	.05	4	6	8	.06	--	.04	.005	.02					
Unused Engine Oil	.0002	.0001	.00001	.0001	.0011	1.36	.0001	.0001	.0001	2.43	.0001	.0006					

TABLE 14
CHASSIS DYNAMOMETER TEST

VEHICLE No.: 0-2547
FUEL: Indolene #15214 No-Lead 91 Octane

Run #	Additive		Vehicle Miles	Test Miles	Test Mode	GRAMS PER MILE PARTICULATE					Run #
	Type	Conc.				Andersen Sampler	Millipore Filter	Andersen + Millipore	Glass Filter, 1 cfm 147mm	47mm	
208A	Baseline	1x	2,886	None	60 mph	.0092	.0030	.0122	.0049	None	208A
208B	"	1x	2,886	None	FCCS	.1027	.0146	.1173	.0293	.0146	208B
208C	"	1x	2,886	None	FCCS	.1467	.0806	.2273	.0659	.0366	208C
213A	"	1x	4,250	None	FCCS	.1247	.0367	.1614	.0367	.0220	213A
213B	"	1x	4,250	None	FCCS	.1833	.0879	.2712	.0769	.0219	213B
213C	"	1x	4,250	None	60 mph	.0058	.0066	.0124	.0042	.0019	213C
218A	"	1x	6,517	None	FCCS	.1173	.0513	.1686	.0366	.0220	218A
218B	"	1x	6,517	None	60 mph	.0031	.0108	.0139	.0066	.0015	218B
218C	"	1x	6,517	None	FCCS	.2199	.0439	.2638	.0403	.0146	218C
227A	"	1x	8,592	None	FCCS	.0586	.0953	.1539	.0513	.0219	227A
227B	"	1x	8,592	None	60 mph	.0051	.0102	.0153	.0067	.0219	227B
227C	"	1x	8,592	None	FCCS	.0659	.1173	.1832	.0696	.0219	227C
233A	"	1x	10,739	None	FCCS	.1100	.0366	.1466	.0386	.0293	233A
233B	"	1x	10,739	None	60 mph	.0025	.0109	.0134	.0060	.0018	233B
233C	"	1x	10,739	None	FCCS	.1100	.0440	.1540	.0626	.0293	233C
244A	"	1x	12,642	None	FCCS	.0513	.1026	.1539	.0879	.0293	244A
244B	"	1x	12,642	None	60 mph	.0043	.0287	.0330	.0082	.0043	244B
244C	"	1x	12,642	None	FCCS	.0586	.1990	.1685	.0916	.0293	244C
250A	"	1x	14,792	14,792	FCCS	.0659	.0733	.1392	.0549	.0293	250A
250B	"	1x	14,792	14,792	60 mph	.0029	.0086	.0115	.0095	.0037	250B
250C	"	1x	14,792	14,792	FCCS	.0733	.0659	.1392	.0623	.0219	250C
253A	"	1x	17,051	-	FCCS	.13199	.19066	.3226	.08066	.02933	253A
253B	"	1x	17,051	-	FCCS	.13933	.16133	.3006	.07333	.02933	253B
253C	"	1x	17,051	-	60 mph	.00704	.0044	.01144	.00778	.00482	253C

TABLE 14 Con't.
EXHAUST GAS ANALYSIS

	% by Volume				Parts per Million				Exhaust Condensate		
Run #	CO_2	O_2	N_2	CO	H.C.	NO_2	NO	NO_x-N_x	ppm HCHO	ppm NH_3	ppm HCHO in exhaust
208A	13.5	2.7	82.6	.10	80	65	1650		336.1	-	.0026
208B	None								104.5	-	
208C	13.1	3.0	82.4	.53	100	120	290		129.8	-	
213A	12.7	4.1	82.2	.03	80	300	275		159.9	-	
213B	13.0	3.8	82.4	.03	120	300	190		192.2	-	
213C	13.4	1.45	82.2	1.48	85	7	1300		180.4		.00021
218A	12.8	3.3	82.2	.92	120	370	275		106.0	-	
218B	13.8	2.25	82.9	.08	65	48	2350		184.7	-	.000153
218C	13.1	2.8	82.3	.90	110	315	220		100.8	-	
227A	12.9	3.2	82.1	.85	115	160	365		160.0	10.4	
227B	13.2	1.9	83.3	.70	75	40	2600		183.0	26.6	.00034
227C	12.8	3.2	81.8	1.35	118	240	360		150.0	14.1	
233A	12.9	3.2	82.3	.72	90	300	125		27.63	17.5	
233B	14.6	2.0	83.0	.10	90	33	2300		294.31	30.8	.00053
233C	12.7	3.1	82.2	1.10	175	210	230		53.58	31.5	
244A	12.3	2.8	83.4	.60	170		39	315	162.02	23.66	
244B	13.4	1.7	83.7	.20	75		-	>2000	232.24	34.19	.00043
244C	12.3	2.8	83.0	.96	167		29	307	189.94	13.10	
250A	12.5	2.1	83.3	1.20	180		350	388	72.4	3.3	
250B	13.4	1.3	84.1	.28	82.5		1680	1793	246.3	6.7	.00050
250C	12.7	1.7	83.3	1.40	190		432	481	84.6	4.0	
253A	12.8	1.6	83.4	1.33	190			260	108.6	6.94	
253B	12.7	1.9	83.3	1.15	170			275	86.7	6.13	
253C	13.0	.85	83.38	1.88	185			1100	119.3	19.98	.00021

TABLE 14 Con't.
ANALYSIS OF EXHAUST PARTICULATE

% on Millipore Filter

Run #	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	% C	% H	% N	benzene Solubles	ppm BAP
208A	2.0	.15	.6	1.0	24.0	8.0	.3	.5	<.03		.03					36	<16
208B	1.0	.04	.12	.09	6.0	2.0	.06	.09	<.05		.005					37	<35
208C													51.0	9.0			
213A	4.0	.04	.7	.3	14.0	7.0	.2	.2	<.01		.03		77.4	9.8		83	<80
213B																	
213C																	
218A	2.0	.05	.4	.4	15.0	7.0	.14	.14	.007	-	.02		47.6	<2		74	230
218B	0.4	.03	.09	.04	3.0	1.8	.02	.07	.07	-	.002		35.8	<2		36	220
218C	2.0	.03	.08	.4	14.0	8.0	.08	.16	.03	-	.04		43.2	<2		90	210
227A	.62	.1	.62	.2	4.8	1.13	.1	.1	.1	.3	.1	2	-			29	710
227B	.53	.1	.32	.1	2.6	.53	.1	.1	.1	.32	.1	3	34.1	<.5		-	-
227C												3	28.0	<.5		32	45
233A	1.4	.1	.4	.8	4.6	1.3	<.04	<.1	<.1	.5	<.1	-				45.8	88
233B	.3	<.1	.1	.1	1.1	.4	<,04	<.1	<.1	<.3	<.1	2.4	34.8	4.8	5.45	262	29
233C													71.9	2.3	1.6		
244A	.7	<.05	.2	.2	2.9	.8	.1	.1	<.05	.3	<.03	<1.9	22.27	8.60	1.83	29	150
244B	.1	<.005	.06	.05	.5	.2	.06	.02	<.05	<.1	<.03	6.3	27.21	5.75	3.48	24	52
244C	.8	<.05	.5	.2	6.2	1.0	.09	.1	<.05	15.0	.04	23.0	9.62	2.49	1.78	15	75
250A	.8	<.05	.4	.4	5.3	1.1	<.1	.1	<.1	.3	<.1	.7	10.7	8.25	22.77	53	96
250B	.2	<.1	.2	.2	2.3	.5	<.1	<.1	<.1	<.3	<.1	.9	17.7	8.0	8.87	27	36
250C	.7	<.1	.5	.4	5.7	1.1	<.1	.1	<.1	.3	<.1	.3	16.8	15.28	23.3	55	74
253A	.3	<.1	.3	.2	1.9	.3	<.05	<.1	<.1	.4	<.1	5.5	9.27	7.50	1.43	28	160
253B	.3	<.1	.3	.1	2.4	.5	<.05	<.1	<.1	.8	<.1	8.5	8.01	8.51	1.10	18	120
253C	.6	<.1	1.2	.3	4.7	1.1	.1	<.1	<.1	2.0	<.1	15.8	24.3	14.25	1.80	28	86
Engine Deposits																	
C. Chamber	1.1	<.01	.03	.09	.1	.9	.01	.01	.05	1.5	.1	5.9	47.1	4.1	.75		70
I. Valve	.4	<.01	.03	.02	.1	1.8	.01	.01	.03	2.9	.01	1.4	52.0	4.6	1.1		1490

Date: 7/9/73

Vehicle No. = D-2547
Fuel Used = Base Fuel No Additive

TABLE 14 Con't.
ENGINE DEPOSITS RATING SHEET

1)	Carburetor Throat Butterfly	No deposits but a very light coating that was black in color.
2)	Intake Manifold	No deposits but black in color.
3)	Exhaust Manifold	Normal deposits black to gray in color.
4)	Intake Valves	Back side of valve had heavy black deposit above normal.
5)	Exhaust Valves	No deposit but dark brown in color.
6)	Combustion Chamber	Very few deposits. Surface was dark tan to black in color.
7)	Spark Plugs	Very few deposits. Surface was dark tan to black in color.

NOTES: The only thing that seemed to be abnormal was the amount of deposit on the back side of the intake valve. Otherwise a very clean engine.

TABLE 15
CHASSIS DYNAMOMETER TEST

VEHICLE No.: D-2548
FUEL: Indolene #15214 No-Lead 91 Octane + Additive A

	Additive					GRAMS PER MILE PARTICULATE					
									Glass Filter, 1 cfm		
Run #	Type	Conc.	Vehicle Miles	Test Miles	Test Mode	Andersen Sampler	Millipore Filter	Andersen + Millipore	147mm	47mm	Run #
209A	A	1x	3,436	0	60 mph	.0118	.0024	.0142	.0054	.0024	209A
209B	"	1x	3,436	0	FCCS	.0807	.0220	.1027	.0513	.0220	209B
209C	"	1x	3,436	0	FCCS	.1614	.0293	.1907	.0623	.0293	209C
215A	"	1x	5,748	2,000	FCCS	.1613	nil	.1613	.0660	.0440	215A
215B	"	1x	5,748	2,000	FCCS	.1613	nil	.1613	.0440	.0220	215B
215C	"	1x	5,748	2,000	60 mph	.0101	.0007	.0108	.0066	.0077	215C
224A	"	1x	7,050	3,302	FCCS	.0879	.0879	.1758	.0806	.0366	224A
224B	"	1x	7,050	3,302	FCCS	.0659	.0219	.0878	.0513	.0219	224B
224C	"	1x	7,050	3,302	60 mph	.0052	.0052	.0104	.0068	.0026	224C
236A	"	1x	9,100	5,352	FCCS	.1100	.0733	.1833	.0476	.0220	236A
236B	"	1x	9,100	5,352	FCCS	.0660	.0660	.1320	.0550	.0220	236B
236C	"	1x	9,100	5,352	60 mph	.0033	.0048	.0081	.0090	.0022	236C
242A	"	1x	10,990	7,242	FCCS	.1246	.0733	.1979	.0535	.0146	242A
242B	"	1x	10,990	7,242	60 mph	.0028	.0047	.0075	.0099	.0244	242B
242C	"	1x	10,990	7,242	FCCS	.0880	.1613	.1906	.0586	.0293	242C
245A	"	1x	13,069	9,633	FCCS	.0733	.1026	.1759	.0843	.0439	245A
245B	"	1x	13,069	9,633	60 mph	.0026	.0020	.0046	.0094	.0026	245B
245C	"	1x	13,069	9,633	FCCS	.1099	.1246	.2345	.1099	.0439	245C
249A	"	1x	15,080	11,332	FCCS	.1393	.0659	.2052	.0659	.0366	249A
249B	"	1x	15,080	11,332	FCCS	.0879	.0733	.1612	.0659	.0366	249B
249C	"	1x	15,080	11,332	60 mph	.0051	.0096	.0147	.0079	.0031	249C
257A	"	1x	17.440	13,692	FCCS	.19066	.0806	.27126	.07333	.0220	257A
257B	"	1x	[illegible],440	13,692	60 mph	.00931	.00969	.0190	.00833	.00349	257B
257C	"	1x	17,440	13,692	FCCS	.11733	.19066	.3079	.10633	.0366	257C

TABLE 15 Con't.
EXHAUST GAS ANALYSIS

	% by Volume				Parts per Million				Exhaust Condensate		
Run #	CO_2	O_2	N_2	CO	H.C.	NO_2	NO	NO_x-N_x	ppm HCHO	ppm NH_3	ppm HCHO in exhaust
209A	13.1	3.1	82.3	.55	125	230	280		149		.00013
209B	14.3	1.4	83.2	.32	100	7.5	2100		136		
209C	None	-	-	-	-	225	230		138		
215A	11.9	5.6	81.4	.19	80	290	250		65		
215B	13.1	3.1	82.2	.72	120	380	245		73		
215C	14.1	2.3	82.7	.04	55	40	2500		126		.00007
224A	13.1	2.8	82.4	.82	205	225	300		76	29.2	
224B	13.5	2.2	82.8	.65	155	180	375		-	-	
224C	13.5	2.7	82.8	.03	55	48	3100		168	35	.00042
236A	12.5	2.3	84.2	.03	170	x	x	141	127.9	28.0	
236B	12.2	2.4	83.7	.76	140	x	x	455	121.4	25.7	
236C	12.4	2.7	83.9	.03	55	x	x	310	340.8	21.8	.00047
242A	12.6	2.1	83.2	1.12	190	-	-	562	99.4	20.4	.00014
242B	13.2	2.2	83.9	.03	60	-	-	2000	197	23.4	
242C	12.5	2.3	83.2	1.12	190	-	-	614	125	13.5	
245A	11.9	1.6	84.5	1.17	230	-	460	552	130.4	4.6	.00039
245B	12.4	1.7	85.0	.030	55	-	>2000	>2000	232.9	8.8	
245C	12.7	1.7	83.3	1.38	220	-	537	618	137.9	3.5	
249A	11.0	4.5	82.4	1.25	205		213	337	119.8	1.2	
249B	12.7	1.9	83.3	1.24	200		466	519	109.1	2.8	.00030
249C	13.1	.8	83.6	1.65	170		2000 T	2000 T	152.4	8.3	
257A	12.7	2.2	83.6	.50	165			334	97.7	1.9	.00020
257B	13.07	.90	83.4	1.66	162			1487	142.3	5.9	
257C	12.9	1.7	83.5	.99	260			385	56.8	4.5	

TABLE 15 Con't.
ANALYSIS OF EXHAUST PARTICULATE

% on Millipore Filter

Run #	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	% C	% H	% N	benzene Solubles	ppm BAP
209A	3.0	.06	.35	.4	21.0	8.0	.1	.4	.01		.01						
209B	3.0	.05	.35	.6	21.0	12.0	.1	.3	.01		.05						
209C																	
215A																52	29
215B																	
215C	5.0	.18	1.8	1.5	71.0	25.0	.8	.5	.2	-	.05		39.8	6.0		23	17
224A	.9	.02	.5	.4	8.0	4.0	.05	.1	.004	-	.01	<5	33.9	6.0		28	310
224B												<4					
224C	2.0	.03	.4	.4	5.0	4.0	.04	.09	.05	-	.007	<8	50.2	5.2		57	180
236A	.9	.1	.4	.3	3.7	3.8	.05	.1	.1	.6	.1	-	35.6	5.16	.01	24.1	30
236B																	
236C	1.0	.1	.5	.3	3.6	1.1	.04	.1	.1	.6	.1	1.3	78.1	11.9	5.08	17.3	140
242A	3.0	.005	.3	2.0	9.0	.2	.1	.3	-	.5	.05	.05	27.07	9.57	2.04	22	32
242B	.6	.0008	.05	.5	10.0	.08	.02	.03	-	.08	.006	.008	20.56	5.47	2.35	58	44
242C	-	-	-	-	-	-	-	-	-	-	-	-	15.52	8.15	.70		
245A	.52	.02	.92	.12	2.6	.63	.03	.09	.41		.08	2.5	16.33	8.15	20.18		
245B	.96	.07	1.4	.28	5.9	1.5	.37	.23	1.0		.17	2.1	26.2	7.32	11.23		
245C	.29	.02	.50	.08	2.0	.46	.07	.07	.29		.06	2.1	17.95	9.77	17.20		
249A	.9	1.7	.4	.4	2.2	.8	<.1	<.1	<.1	<.3	<.1	.3	19.75	10.2	22.30		<50
249B	.7	<.1	.4	.3	5.2	.9	.1	.1	<.1	<.3	<.1	<.3	14.2	16.22	27.3	58	140
249C	.2	<.1	.2	.1	2.0	.4	<.1	<.1	<.1	<.3	<.1	<.3	52.0	12.6	18.52	46	35
257A	1.1	<.1	.8	.5	5.7	1.0	.05	<.1	<.1	1.1	<.1	5.8	23.5	11.91	2.66		<30
257B	.3	<.1	.3	.2	1.8	.4	<.05	<.1	<.1	.5	<.1	2.5	25.3	12.2	2.70		127
257C	.2	<.1	.2	<.1	1.5	<.3	<.05	<.1	<.1	<.3	<.1	4.5	17.4	13.5	2.81		31
Engine Deposits																	
C. Chamber	1.2	.02	.2	.2	.4	.9	.09	.01	.1	3.0	.02	6.2	48.2	3.7	2.26		3500
I. Valve	1.1	<.01	.07	.03	.3	.2	.02	.01	.1	1.0	.01	.8	72.2	7.8	3.06		5500

Date: 7/12/73

Vehicle No. = D-2548
Fuel Used = Additive A

TABLE 15 Con't.
ENGINE DEPOSITS RATING SHEET

1) Carburetor Throat Butterfly	Clean, bare metal. No deposits or discoloration.
2) Intake Manifold	Clean with no deposits or discoloration but the surface was wet with a film coating.
3) Exhaust Manifold	Light coating of black carbon with no buildup of deposits.
4) Intake Valves	Some buildup of a black deposit that had a gooey consistancy was present on the back side of all valves.
5) Exhaust Valves	A thin reddish coating was present on the back side of valve while the tops were whiteish.
6) Combustion Chamber	Thin deposit brown to black in color. Coating was equal on all cylinders.
7) Spark Plugs	No deposits with a dark brown color. Appeared cleaner than normal.

NOTES: In general it appeared to be the cleanest engine of the three with no heavy deposit buildup.

TABLE 16
CHASSIS DYNAMOMETER TEST

VEHICLE No.: D-2549
FUEL: Indolene #15214 No-Lead 91 Octane + Additive B

	Additive					GRAMS PER MILE PARTICULATE					
									Glass Filter, 1 cfm		
Run #	Type	Conc.	Vehicle Miles	Test Miles	Test Mode	Andersen Sampler	Millipore Filter	Andersen + Millipore	147mm	47mm	Run #
207A	B	1x	3,529	0	FCCS	.0073	.0366	.0439	.0623	.0293	207A
207B	"	1x	3,529	0	FCCS	.1099	.0513	.1612	.0586	.0293	207B
207C	"	1x	3,529	0	60 mph	.0105	.0019	.0214	.0071	.0023	207C
216A	"	1x	6,051	2,000	FCCS	.2493	.0293	.2786	1.444	.3666	216A
216B	"	1x	6,051	2,000	60 mph	.0074	.0089	.0163	.0202	.0124	216B
216C	"	1x	6,051	2,000	FCCS	.2053	.0219	.2272	.1026	.0293	216C
230A	"	1x	8,015	3,964	FCCS	.0440	nil	.0440	.0807	.0367	230A
230B	"	1x	8,015	3,964	FCCS	.0587	nil	.0587	.0807	.0367	230B
230C	"	1x	8,015	3,964	60 mph	.0050	.0192	.0242	.0196	.0132	230C
237A	"	1x	10,026	5,975	FCCS	.0660	.1026	.1686	.0953	.0513	237A
237B	"	1x	10,026	5,975	60 mph	.0050	.0465	.0515	.0265	.0166	237B
237C	"	1x	10,026	5,975	FCCS	.0733	.1100	.1833	.1633	.0880	237C
243A	"	1x	11,890	8,361	FCCS	.0659	.1833	.2492	.0953	.0733	243A
243B	"	1x	11,890	8,361	60 mph	.0035	.0362	.0397	.0218	.0132	243B
243C	"	1x	11,890	8,361	FCCS	.1026	.1833	.2859	.1539	.1173	243C
251A	"	1x	14,030	9,979	FCCS	.0879	.4913	.5792	.1796	.0953	251A
251B	"	1x	14,030	9,979	60 mph	.0078	.0905	.0983	.0412	.0282	251B
251C	"	1x	14,030	9,979	FCCS	.1393	.3960	.5353	.1759	.0953	251C
						(New Spark Plugs)					
251D	"	1x	14,030	9,979	60 mph	.0034	.0386	.0420	.0214	.0134	251D
258A	"	1x	16,407	12,356	FCCS	.1760	.08067	.2566	.0550	.0440	258A
258B	"	1x	16,407	12,356	60 mph	.00779	.01113	.01892	.01614	.0129	258B
258C	"	1x	16,407	12,356	FCCS	.2795	.2860	.5655	.2240	.1320	258C

*NOTE: For Runs 258A and B: Air conditioner in dilution tube room was off temperature of 96°F in room. Normal temperature of 75°F - possibility of a low particulate collection due to temperature of dilution tube starting off above normal. Run 258C = 78°F.

TABLE 16 Con't.
EXHAUST GAS ANALYSIS

	% by Volume				Parts per Million				Exhaust Condensate		
Run #	CO_2	O_2	N_2	CO	H.C.	NO_2	NO	NO_x-N_y	ppm HCHO	ppm NH_3	ppm HCHO in exhaust
207A	n.g.	-	-	-	-	90	185		142		
207B	13	3.2	82.2	.7	140	280	310		160		.00011
207C	14.3	1.5	83.1	.16	100	15	2000		161		
216A	13.1	2.8	82.3	.82	225	300	300		195		
216B	13.9	2.4	82.7	.74	155	28	625		478		.00037
216C	13.1	2.9	82.3	.74	240	260	250		246		
230A	12.9	2.8	82.1	1.31	320	170	250		310	20.6	
230B	n.g.	-	-	-	-	-	-		219	23.7	.00052
230C	13.8	2.2	83.0	.03	90	65	2800		297	53.0	
237A	12.1	2.4	83.3	1.3	380	-	220	465	347.06	26.3	
237B	13.5	1.5	84.0	.17	190		2000	2000	702.29	35.9	.0012
237C	12.6	1.8	83.3	1.38	370		360	440	271.95	23.7	
243A	11.9	1.9	82.8	2.88	500		402	382	173.83	23.42	
243B	13.4	1.6	83.9	.20	245			2000	703.4	60.76	.0014
243C	12.0	2.0	82.6	2.45	555		342	371	223.51	18.02	
251A	11.6	3.0	82.6	1.93	980		229	275	385.2	3.0	
251B	12.7	2.53	83.3	.45	1354		1660	1639	337.8	14.0	.0006
251C	12.0	1.9	83.9	2.26	500		293	314	271.2	3.9	
						(New Spark Plugs)					
251D	13.3	1.45	83.8	.48	295		1862	1909	-	-	
258A	12.7	1.5	83.4	1.48	355			273	196.7	9.59	
258B	13.0	1.15	82.8	2.18	447			1170	301.2	6.79	.00035
258C	12.1	2.1	82.9	2.04	450			261	126.2	9.09	

TABLE 16 Con't.
ANALYSIS OF EXHAUST PARTICULATE

% on Millipore Filter

Run #	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	% C	% H	% N	benzene Solubles	ppm BAP
207A	10.0	.06	.3	.4	16.0	9.0	.6	.3	<.01		.03		97.0	16.7			
207B	4.0	.06	.3	.3	9.0	7.0	.1	.2	<.01		.02		-	-	-	28	25
207C																32	250
216A	4.0	.18	.35	.6	18.0	5.0	40.0	.4	<.01		.05		<5	<2		2.4	4
216B	3.0	.17	.45	.8	20.0	5.0	60.0	.3	<.01		.05					13	12.5
216C																-	-
230A	10.0	.1	.10	.02	.58	.30	.22	.1	.1	.6	.1	2.0	47.0		3.5	-	-
230B	.22	.05	.14	.05	.88	.40	25.9	.05	.05	.22	.05	3.0	-	-	-	38	45
230C												3.1	23.1	-	1.6	18	36
237A																-	
237B	.1	<.1	.1	<.1	.5	.3	12.3	<.1	<.1	<.3	<.1	3.0	18.79	1.78	2.41	20.0	<12
237C	.6	<.1	.5	.2	3.2	1.1	11.5	<.1	<.1	.6	<.1		18.2	5.3	.45	11.9	<6
243A	.7	<.1	.3	.2	2.3	.6	4.3	.1	<.1	.3	<.1	<0.75	29.32	10.31	.77	35	150
243B	.1	<.1	.1	<.1	.5	.2	14.2	<.1	<.1	<.3	<.1	2.6	18.55	3.27	1.93	12	62
243C	.5	<.1	.3	.2	1.8	.6	7.1	<.1	<.1	.3	<.1	3.3	24.79	6.78	.25	19	160
251A	.1	<.1	.09	<.1	.8	.2	1.4	<.1	<.1	.3	<.1	4.6	9.59	3.95	8.76	13	28
251B	.03	<.01	.02	.02	.2	.1	5.5	<.01	<.01	.1	<.01	2.8	34.45	5.97	3.58	38	16
251C	.1	<.1	.11	<.1	.9	.2	2.8	<.1	<.1	.3	<.1	6.0	9.59	4.63	7.01	9.5	30
251D	.07	<.01	.05	.02	.4	.2	8.0	<.01	<.01	.2	<.01	5.8	17.1	4.05	6.88	16	24
258A	.7	<.1	.6	.4	5.2	1.1	6.8	<.1	<.1	.4	<.1	3.8	39.3	25.6	9.6		75
258B	.3	<.1	.2	.1	1.7	.6	26.9	<.1	<.1	.3	<.1	2.4	20.2	5.5	3.68		144
258C	.2	<.1	.2	<.1	1.3	.3	4.5	<.1	<.1	<.3	<.1	4.2	0.2	6.4	1.5		84
Engine Deposits																	
C. Chamber	.3	<.01	.02	.06	.4	2.2	11.7	.01	<.1	4.0	<.01	10.9	28.13	2.04	0.65		307
I. Valve	1.0	.02	.08	.07	.9	1.4	4.1	.01	<.1	3.0	<.01	5.4	41.72	3.37	1.49		1950

Vehicle No. = D-2549
Fuel Used = Additive B

TABLE 16 Con't.
ENGINE DEPOSITS RATING SHEET

1)	Carburetor Throat Butterfly	Dark gray color, clean with no deposit buildup, considered normal.
2)	Intake Manifold	Black color, clean and dry with no deposits, considered normal.
3)	Exhaust Manifold	Black color, carbon coated but dry, considered normal.
4)	Intake Valves	Considerable buildup. Black deposit was present on the back side of all intake valves.
5)	Exhaust Valves	Were tan in color with a thin black coating. There were no deposits as such.
6)	Combustion Chamber	The quantity of deposits appeared to be normal although some cylinders had more deposits than others.
7)	Spark Plugs	The deposits were tan in color and below normal in amount.

NOTES: Deposits in the combustion chamber were tan in color. When the deposits were scraped from the piston tops, most of the deposit or coating would come off, leaving the bare aluminum.

Some spark plug fouling was noted.

TABLE 17

MASS MEDIUM EQUIVALENT DIAMETER ENGINE STAND RUNS

Run #	Additive	Conc.	Mode*	cutoff % 50%	80%
239 A	B	1X	CS	1.5	3.7
239 B	B	1X	HS	< .5	1.4
239 C	B	1X	HS	< .5	1.0
241 A	B	3X	CS	.9	2.3
241 B	B	3X	HS	< .5	1.0
241 C	B	3X	HS	< .5	.7
240 A	Baseline	1X	CS	1.1	1.6
240 C	Baseline		HS	< .5	2.3
234 A	A	1X	CS	1.0	4.3
234 B	A	1X	HS	1.6	4.0
234 C	A	1X	HS	1.0	3.2
238 A	A	3X	CS	.9	3.0
238 B		3X	HS	.55	4.1
238 C		3X	HS	< .5	2.2

* CS = Cold Start, 23 minute Federal cycle
HS = Hot Start, 23 minute Federal cycle
All % cutoff values in microns

TABLE 18

MASS MEDIUM EQUIVALENT DIAMETER VEHICLE RUNS

Baseline				Additive A				Additive B			
Run #	Mode*	50%	80%	Run #	Mode*	50%	80%	Run #	Mode*	50%	80%
208 A	60	1.3	3.8	209 A	60	1.0	4.2	207 A	CS	< .5	3.0
208 B	CS	.9	5.0	209 B	CS	.9	2.5	207 B	CS	.55	1.5
208 C	CS	< .5	1.5	209 C	CS	1.0	3.0	207 C	60	1.2	3.2
213 A	CS	1.4	4.0	215 A	CS	1.0	2.3	216 A	CS	.7	2.0
213 B	CS	.6	3.5	215 B	CS	1.6	3.8	216 B	60	< .5	1.5
213 C	60	< .5	2.0	215 C	60	1.3	3.2	216 C	CS	1.1	2.4
218 A	CS	.6	2.0	224 A	CS	< .5	1.7	230 A	CS	1.3	3.8
218 B	60	< .5	.55	224 B	CS	.8	3.0	230 B	CS	1.2	3.6
218 C	CS	1.2	3.3	224 C	60	< .5	2.5	230 C	60	< .5	< .5
227 A	CS	< .5	1.3	236 A	CS	< .5	1.8	237 A	CS	< .5	1.8
227 B	60	.5	1.0	236 B	CS	.5	1.1	237 B	60	< .5	.5
227 C	CS	< .5	1.8	236 C	60	< .5	3.7	237 C	CS	< .5	.7
233 A	CS	.7	2.5	242 A	CS	.6	2.8	243 A	CS	< .5	.7
233 B	60	< .5	< .5	242 B	60	< .5	1.0	243 B	60	< .5	< .5
233 C	CS	.7	2.3	242 C	CS	< .5	1.1	243 C	CS	< .5	1.0
244 A	CS	< .5	2.0	245 A	CS	< .5	2.0	251 A	CS	< .5	< .5
244 B	60	< .5	< .5	245 B	60	< .5	2.5	251 B	60	< .5	< .5
244 C	CS	< .5	1.5	245 C	CS	< .5	2.0	251 C	CS	< .5	< .5
250 A	CS	< .5	1.8	249 A	CS	.55	1.8	258 A	CS	.6	3.0
250 B	60	< .5	.7	249 B	CS	.55	2.6	258 B	60	< .5	1.4
250 C	CS	< .5	2.0	249 C	60	< .5	.6	258 C	CS	< .5	2.1
253 A	CS	< .5	1.1	257 A	CS	.9	3.3				
253 B	CS	< .5	2.1	257 B	60	< .5	1.7				
253 C	60	.55	3.0	257 C	CS	< .5	1.7				

* CS = Federal cycle 23 minute cold start   60 = 60 mph steady state, 2 hours

All % cutoff values in microns

4. Particulate Mass-Size Distribution

The mass medium equivalent diameter (MMED) for the engine stand and vehicle tests are summarized in Tables 17 and 18. Cut-off values of both 50% and 80% are used. In general, the particulate mass-size distributions range from Additive B, giving the smallest particles while Additive A gave the largest, with the baseline in between. The 50% cut-off was quite inconclusive since most 50% values fell below the smallest measured separation (.55μ). The 80% cut-off showed much more of a trend toward the conclusion drawn above. The mass distribution plots are found in Appendix A, in order of run number.

It does not appear that using the additive at 3 times the recommended levels caused any noticeable difference in MMED. The complete set of MMED graphs are in Appendix A.

5. Particulate Morphology as Studied by Scanning Electron Microscope

Samples collected from the vehicles were studied using the scanning electron microscope to determine if there were differences in the physical or chemical nature of the individual particles. Several conclusions were drawn, as follows:

a. Additive B tends to produce a very fine particle size with no evidence of flakes, rods, crystals, or flower-like material.

b. The base fuel tends to produce more spherical particles and little crystalline or rod-like material.

c. Additive A tends to produce more crystalline material, porous rod-like material, and flower-like clumps.

d. A flake-like material, never previously encountered in exhaust particulate photographs, was observed in the base fuel and with Additive A.

e. The particulate encountered using Additive A was high in sulfur, while Additive B gave particulate high in manganese.

The data reported as a result of the SEM work must be considered incomplete because of a lack of individual particulate identification. In order to chemically identify the individual particles and correlate chemistry with morphology, it is essential that the material be collected on a substrate that will interfere neither with the chemical nor morphological analyses. The most appropriate substrate for use in the Andersen sampler is thin, flat, polished, and pure graphite. Unfortunately, the irregular topography of the graphite substrates used prevented the measurement of representative particle morphology. As a consequence, the morphological studies were carried out on Au-Pd coated particulate collected on glass cover slips which precluded accurate chemical analyses. The chemical analyses were carried out on aggregates of particles scraped from the collection plates onto the graphite substrates, a process which prevents chemical identification of individual particles.

The complete results of the qualitative chemical analyses of the aggregates of particulate are summarized in the attached table and the predominant differences in chemistry are as follows:

TABLE 19

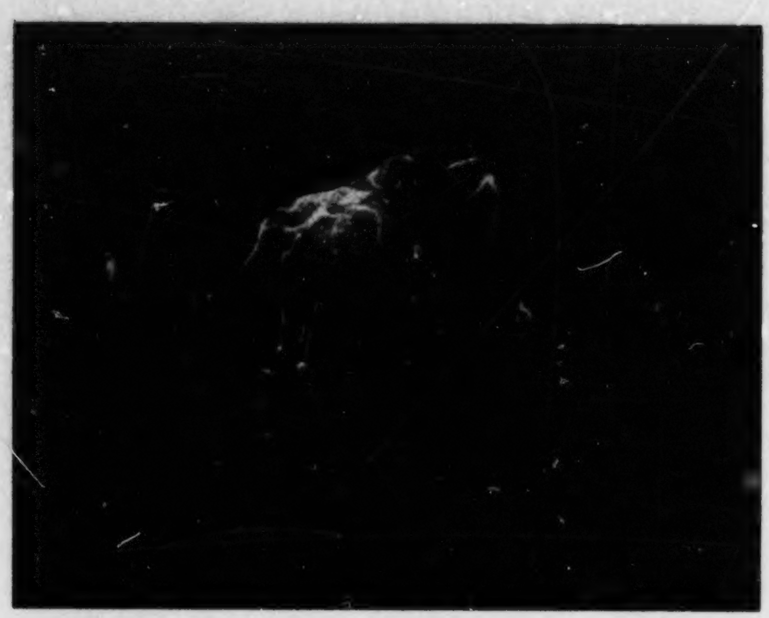
Element	Base Fuel	Additive A	Additive B
Pb	high	none	high
Br	low	none	none
Zn	none	low	low
Ca	low	low	low
S	low	high	low
Mn	none	low	high

The data implies that Additive A somehow reduces or eliminates Pb from the auto exhaust particulate, since the base fuel in all series contained Pb. The Additive B does not produce this effect. Br was only found in the base fuel particulate. Both additives lead to low Zn content in the particulate (none in base fuel particulate). Additive A gives particulate relatively high in S, while Additive B produces particulate high in Mn. Mn was not found in the base fuel particulate and was only present at a low level in one other sample.

The only difference in chemistry between plates would appear to be a slight tendancy for higher concentrations of some elements (Si, S, Ca) to be found in the particulate on Plate 5 (pg 110,111,112). Another nebulous effect is an apparent increase in Pb and S when progressing from a cold to a 60 mph start.

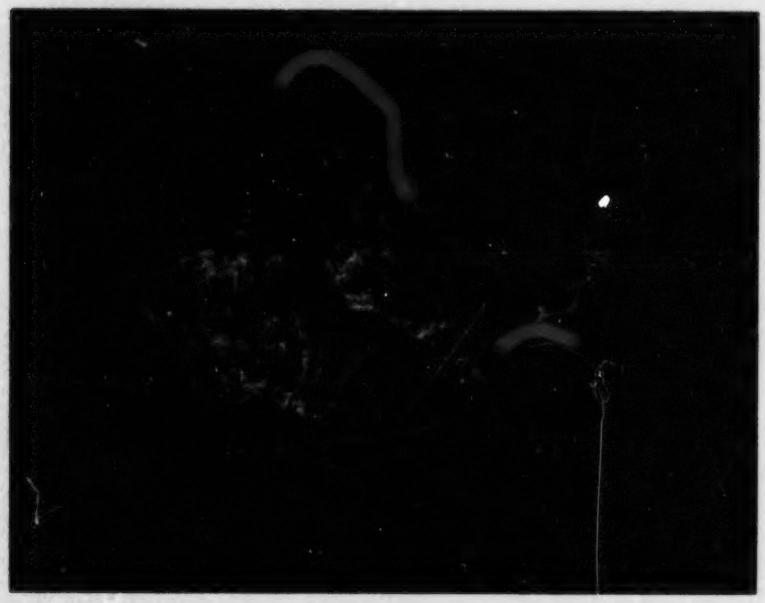
The morphological variations are so large within a particular sample that it is somewhat hazardous to compare samples and generalize. The scanning electron micrographs are attached and documented in Figures 20 through 33. Compared to the base fuel sample Additive A appears to produce more crystalline material, more of the porous rod-like material, and perhaps more of the flower-like clumps. The base fuel sample appears to produce more spherical particles and some crystalline or rod-like material. The 60 mph steady-state baseline exhibits a small particle size with a relatively uniform particle distribution. Additive A and the baseline both contain some thin, flake-like material not previously encountered. The series of Additive B samples exhibit a finer particle size than the baseline or Additive A with no evidence of flakes, flower-like material, crystalline material, or rods. Additive B Federal cycle cold start particulate appears more electron-transparent than the other samples.

Figure 20



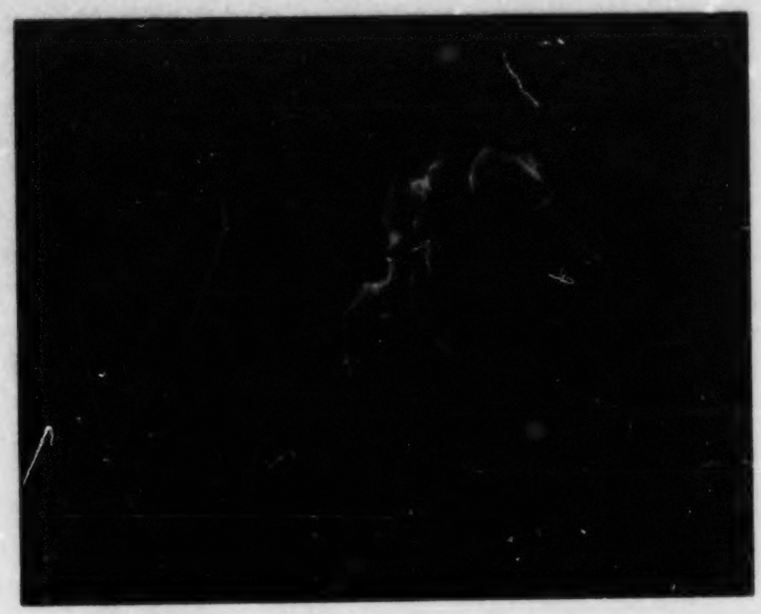
Baseline, Cold Start, 5000x
Plate 2, Andersen Separator

Figure 21



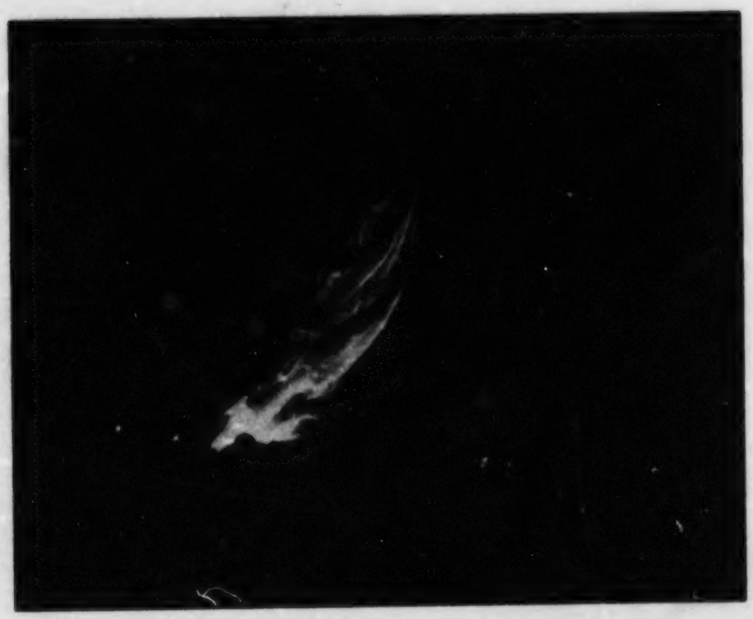
Baseline, Cold Start, 5000x
Plate 2, Andersen Separator

Figure 22



Baseline, Cold Start, 2000x
Plate 2 Andersen Separator

Figure 23



Baseline, Cold Start, 2000x
Plate 2 Andersen Separator

Figure 24

Additive A, Cold Start, 2000x
Plate 2 Andersen Separator

Figure 25

Additive A, Cold Start, 2000x
Plate 2 Andersen Separator

Figure 26

Additive A, Cold Start, 10,000x
Plate 2 Andersen Separator

Figure 27

Additive A, Cold Start, 10,000x
Plate 2 Andersen Separator

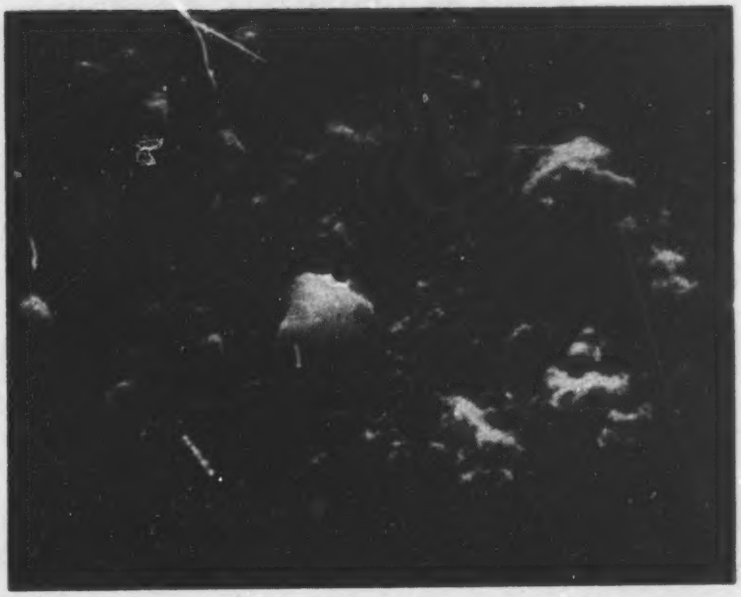
Figure 28

Additive A, Cold Start, 10,000x
Plate 2 Andersen Separator

Figure 29

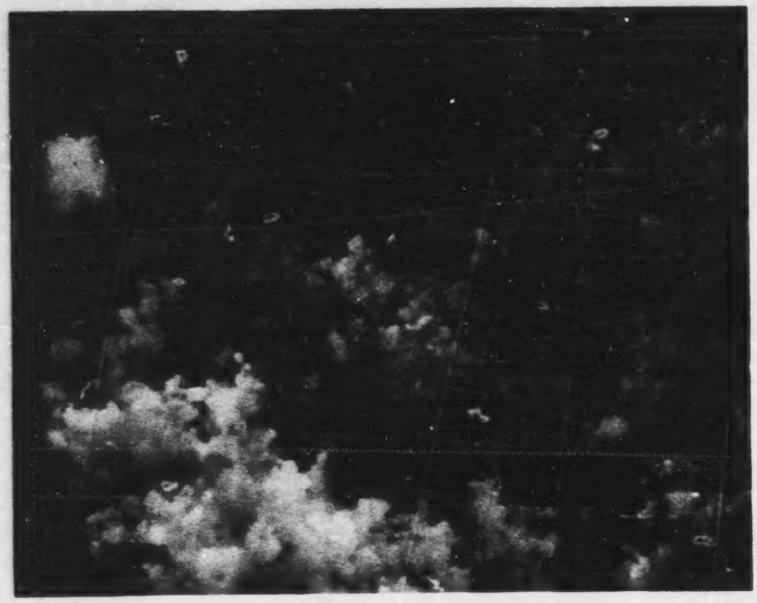
Additive B, Cold Start, 2000x
Plate 5   Andersen Separator

Figure 30



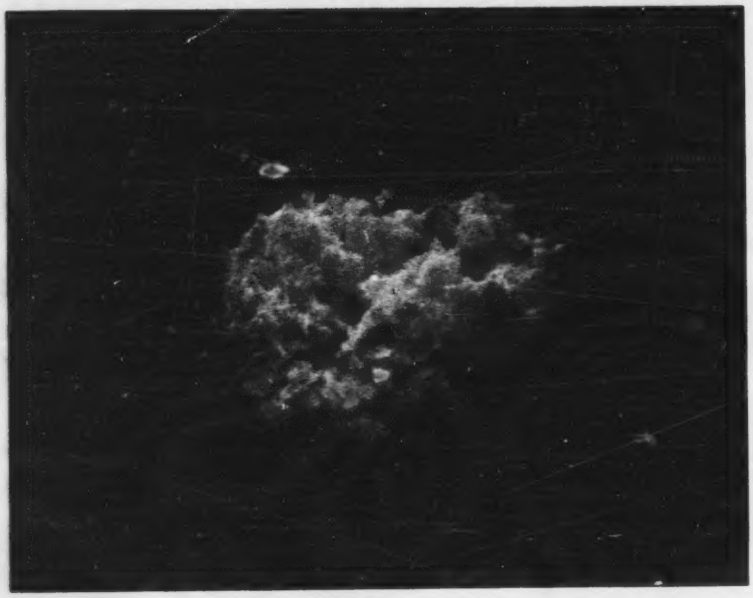
Additive B, Cold Start, 10,000x
Plate 5 Andersen Separator

Figure 31



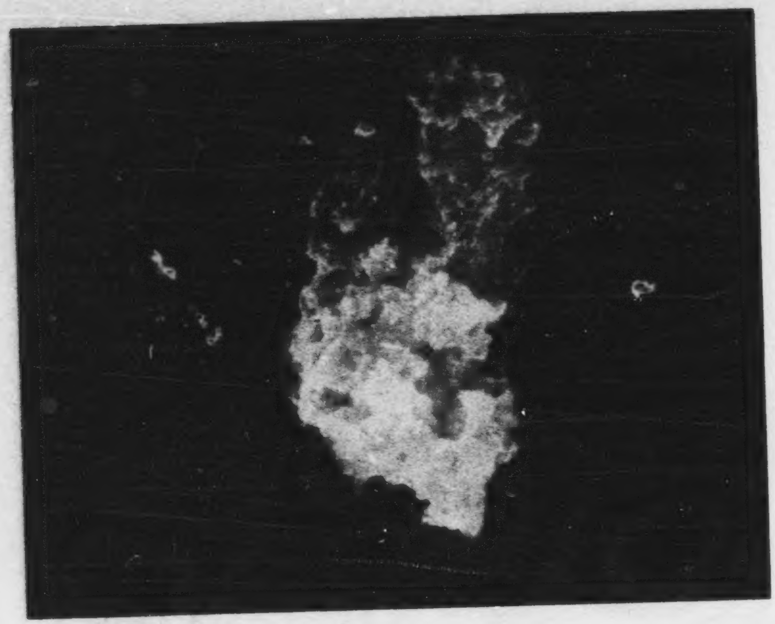
Additive B, Cost Start, 2000x
Plate 5 Andersen Separator

Figure 32



Additive B, Cold Start, 2000x
Plate 5 Andersen Separator

Figure 33



Additive B, Cold Start, 5000x
Plate 5 Andersen Separator

VI. FUEL ADDITIVE SURVEY

Part of the effort in this contract involved a study of the trends which might be apparent concerning the type and usage rate of future fuel additives. Bay refineries, Leonard Oil Co., American Oil, Phillips Petroleum, and Union Oil Co. were contacted in April, 1972, and the subject of new additives was discussed in detail. In addition, a survey of the available current literature was made. Most sources were quite reluctant to discuss additives other than those currently available, in any but the most general terms. It appears that most research in this area is guarded quite closely, since any development of a new additive can be of more benefit to the developer if it remains proprietary as long as possible. Questions concerning trends of future additive research were invariably met with the response "we really don't know".

Following is a summary of discussions on currently used fuel additives, segregated by functionality of the additive. None of the companies contacted were willing to speculate on the future of antiknock additives, assuming that lead alkyls will be prohibited. No discussion of antiknocks is made for that reason.

A. DYES

Dyes have for years been added to gasoline at the recommendation of the Surgeon General. The color serves as a warning that the gasoline contains lead. Oil soluble solid dyes are generally azo compounds and amino and oxygenated aromatics, such as benzene, naphthalene or anthracene derivatives. Thus, other than carbon and hydrogen, the only other elements present in gasoline dyes are oxygen and nitrogen. Liquid dyes are currently becoming more popular because of their ease of handling in automatic in-line gasoline blending. We are not familiar with the chemistry of liquid dyes but believe that they are quite similar to the solid dyes. Dyes are added to gasoline at the 1-6 ppm range. Suppliers are Morton Chemicals, Du Pont and Ethyl. Some examples are Du Pont Red B Liquid and Du Pont Orange Liquid. In the future dyes may well be used to a lesser extent than they are currently. In an EPA proposal for removing lead from gasoline (Federal Register, February 23, 1972) refiners would be required to supply by 7/1/74, an unleaded gasoline which contains no dye. Even though dyes are expensive, people in the petroleum industry, especially those in Marketing and Transportation, have gotten accustomed to having gasoline dyed. The color is helpful as a means to distinguish between the different grades of gasoline and midbarrel products. Thus, barring legislation against them, dyes will probably continue to be used.

B. ANTIOXIDANTS

Other than lead alkyls, antioxidants were the first additives used in gasoline. Antioxidants became necessary when cracking methods were introduced into refining. Olefins, which are formed during the cracking process, are susceptible to liquid-phase oxidation. One of the products of the oxidation process is an insoluble gum. The gum can clog fuel filters and lines, carburetor jets, intake manifolds, and valve ports and can add to intake valve tulip area deposits. As this oxidation takes place via a free radical mechanism, materials which donate a hydrogen atom can terminate the formation of the intermediate peroxy radicals.

Thus aromatic amines and phenols are good gasoline antioxidants. The most commonly used materials are N,N'-di-sec-butyl-p-phenylenediamine, N-n-butyl-p-aminophenol, and 2,6-di-tert-butyl-4-methylphenol. Antioxidant dosages range from 8-40 ppm. The phenylenediamine type inhibitor is popular because it also acts as a catalyst for sweetening gasoline. Over the years the percentage of olefins in gasoline has decreased and thus the amount of antioxidants required has decreased. However, as the olefin content has gone down the percentage of higher octane aromatics has gone up. Aromatics can also form peroxides. Although the aromatic peroxides do not contribute to gum formation, they do react with the lead alkyls. The result is hazy fuel and sometimes precipitates of lead salts. Thus antioxidants are still required, although at lower concentrations than for gum prevention. In the future as lead alkyls are removed from gasolines, the need for antioxidants will be even less. There are many suppliers of antioxidants such as Du Pont, Hercules, Productol, Ethyl, Koppers, Shell, and Eastman.

C. METAL DEACTIVATORS

Trace quantities of metals in gasoline, especially copper, catalyze the oxidation of the fuel. As little as 0.1 ppm copper can be troublesome. Copper gets into the gasoline through either a copper sweetening process or merely from copper or brass fittings used in refining and distribution. Copper can be deactivated by the use of a chelating agent. The most common chelating agent is N,N'-disalicylidene-1,2-diaminopropane. This material is sold by several additive suppliers under as many different trade names. Examples are Du Pont DMD-2, Ethyl MDA, Tretolite Kuplex 60, and Eastman Tenemene 60. Another metal deactivator which is used is Du Pont Metal Suppressor, a carboxylic acid salt of

1-salicylalaminoquanidene. Metal deactivators are used at concentrations of 1-12 ppm in conjunction with antioxidants. Many refiners no longer use metal deactivators, as the trace metals content of their gasolines may be below the level necessary to act as a catalyst. Also, as with antioxidants, as the olefins content of gasoline decreases, the need for a metal deactivator diminishes.

D. SURFACE-ACTIVE AGENTS

Surface-active agents (surfactants) are the newest type of additives to be used in gasoline. At very low concentrations these additives can prevent fuel system corrosion, prevent and remove carburetor deposits, prevent and remove intake manifold deposits, and prevent carburetor icing.

1) Rust Preventing Additives

Extremely low concentrations of certain surfactants are very effective in preventing corrosion in wet gasoline systems. Water, the result of tank breathing, is almost always present in gasoline terminal storage tanks, gas station tanks and vehicle fuel tanks. Materials which contain a polar group and a long hydrocarbon chain can be absorbed in a close-packed monomolecular layer on metal surfaces. If the film is impervious to water, then rust protection is achieved. Carboxylic acids, alcohols, amines, sulfonates, and phosphoric acid salts of amines are all effective rust inhibitors. Commercial rust inhibitors include Du Pont AFA-1, Apollo PRI-19, Nalco 5400, Vanderbilt Nasul LP, Tretolite Tolad T-245, UPO Unicor PL, Edwin Cooper Hitec E-534, and Lubrizol 541. These surfactants are quite effective in the range 4-40 ppm. As it is almost impossible to completely eliminate water from liquid fuel systems it is most likely that the use of surfactant type rust inhibitors will continue for some time.

2) Gasoline Detergents

Some surfactants are very effective in preventing and removing deposits which form in the throttle bore area of a carburetor. Such deposits have been a problem since the widespread use of 2-barrel carburetor V-8 engines began in 1955. In current automobiles with their many emission control devices the accumulation of deposits has become even more severe. Detergent additives have been in use for almost 20 years. The most effective ones are amines and amine phosphate salts.

Extensive research efforts have been directed toward finding more effective detergents. The recent trend has been to higher concentrations of polyamine materials. Unless legislation forces the removal of nitrogen containing additives from use in gasoline, it appears that because these types of additives are so effective they will continue to be used. Current highly effective detergent additives include: alkyl amine phosphates, e.g. Du Pont DMA-4, Ethyl MPA-90, and Gulf Agent 724; alkyl amines, e.g. Union Oil NR-76, Enjay Paradyne 55, and Humble HTA-71; polybutene polyamines, e.g. Amoco 575, Lubrizol 8101, and Oronite OGA-472. Detergent concentrations range from 15 to 150 ppm.

3) Intake Manifold Deposits

Some surfactants, primarily the high molecular weight polymer dispersants, are effective in preventing and removing intake system deposits. In this case the cleaning action of the surfactant is not a result of coating the metal surface but appears to be the result of softening the deposits so that they then slough off. A more effective means of removing and preventing the formation of these deposits is through the use of an effective dispersant plus a high concentration (0.05-0.5 volume %) of a low volatility lubricating oil. In this case the dispersant softens the deposits and the top cylinder oil serves as a flux to "wash" the metal surface clean. Examples of dispersant gasoline additives are: Lubrizol 580 and 8101, Enjay Paradyne 501, Amoco 575, and Oronite OGA-472. In the past two years there has been a trend towards the use of dispersant additives and a smaller yet significant trend towards the use of top cylinder oils.

4) Deicing Additives

Two types of icing occur in automobiles; freezing of water in the fuel and carburetor icing. Ice formation in the fuel can be eliminated through the use of freeze point depressants such as alcohols, glycols or dimethylformamide. These materials are added to the gasoline. However, because they are more soluble in water they move into the aqueous phase and lower its freezing point. Freeze point depressants are used at concentrations up to 2 volume %.

Carburetor icing occurs in cool, damp weather when moisture in the air freezes on metal surfaces in the carburetor throat and on the throttle blade. Stalling because of carburetor icing can be reduced through the use of surfactant additives. Such materials coat the throttle plate and carburetor walls so that ice crystals will not adhere. The surfactants can also interfere with ice crystal growth causing a snow-like ice which is easily blown off of the metal surfaces. Effective surfactant deicers included Du Pont DMA-4 and Ethyl MPA-90. These deicers are effective in the 20-100 ppm range. Because engines in late model cars are designed to heat the intake air rapidly, the problem of stalling because of carburetor icing will not be as critical in the future as it has been in the past. Thus, additives which function only as deicers will probably not be used much in the future.

E. "CANNED" ADDITIVES

"Canned" additives, those which are offered for sale in service stations and retail stores, are a multi-million dollar per year business. Though many of these additives claim reduced pollution, increased mileage, higher horsepower, etc., in most cases these claims are unfounded. The majority of "canned" additives are top cylinder oils or solvents or both. Those which contain surfactant materials are similar to the additives mentioned above, although generally surfactants, if present at all, are present at extremely low concentrations. However, because there is obviously a market for these additives, it seems reasonable to assume that their use will continue.

F. 2-CYCLE ENGINES

Lubrication of 2-cycle engines takes place via the gasoline. Therefore, gasolines for 2-cycle engines contain the lubricating oil additives. These additives are a combination of materials which consist mostly of either a calcium sulfonate or amine-type dispersant. Examples are Lubrizol 981 and Oronite 340K, respectively. The concentration of lubricating oil in gasoline varies from 2 to 4 percent. The concentration of additive in the gasoline is in the 0.1 to 0.4 percent range. Because of recent water pollution legislation the lubricating oil concentration will soon be reduced to 1%. Also in the future the calcium sulfonates may be replaced altogether by the amine-type ashless dispersants.

G. SUMMARY AND CONCLUSION

Extensive research efforts by several companies over many years have resulted in the gasoline additives which are currently in use. Research is continuing in an effort to find even more effective additives. However, current technology still indicates that the amine, amine phosphate and amine polymer surfactants are the most effective additives for controlling many of the problems associated with today's internal combustion engines. As new applications for additives are sought possibly a new and different type of additive will be found. An example of a new use for additives is Humble's HTA-71. This additive is claimed to control surge, a problem which is becoming more common in today's leaner running engines. Here again HTA-71 is an alkyl amine surfactant. Thus for the naturally aspirated internal combustion engine, we believe that gasoline additive types currently in use will remain in use for some time.

VII. CONDENSATE COLLECTION AND ANALYSES

A modification to Contract 68-01-0332 included the generation and collection of exhaust gas condensate samples for use in biological studies. The condensate was collected and analyzed using techniques discussed in Sections III-C, and III-I 7 a,b, respectively. A 1972 350 CID Chevrolet engine was used. This engine had previously been broken in and operated on continuous 23-minute Federal cycles. The conditions of operation for the collection of the condensate samples was identical to that used for the particulate studies. Half of the samples were taken using both cold start and hot start 23-minute cycles, while half were taken at 60 mph steady-state conditions. The runs were made using the Indolene baseline fuel and fuel containing 1.87 g/gal. of Additive A, and .25 g/gal. of Additive B, based on manganese. Standard gaseous analyses were made, as well as particulate measurements and analyses. The condensate analyses data is reported in Table 20, and the particulate data is in Table 21. Mass size distribution is shown in Figures 34 through 39.

The samples were sent to the University of Nebraska for use in animal health studies.

TABLE 20
HCHO and NH_3 Analyses of Exhaust Condensate

Sample #	Additive	Test Mode	ppm HCHO	ppm NH_3	Run #
98G	none	FCCS	453	10.4	254A
99G	none	60 mph	263	15.6	254B
100A	none	FCHS	340	12.0	
100B	none	60 mph	252	12.8	
100C	none	FCHS	434	13.6	
100D	none	60 mph	352	15.8	
100E	none	FCHS	349	8.4	
100F	none	FCCS	385	12.0	
100G	none	60 mph	304	12.0	
100H	none	FCHS	403	12.0	
100I	none	60 mph	315	11.6	
101G	OGA-472	FCCS	226	6.8	255B
102G	OGA-472	60 mph	351	7.2	255A
103A	OGA-472	FCHS	330	10.0	
103B	OGA-472	60 mph	274	12.0	
103C	OGA-472	FCHS	403	8.4	
103D	OGA-472	60 mph	278	11.2	
103E	OGA-472	FCHS	209	11.2	
103F	OGA-472	60 mph	334	9.2	
103G	OGA-472	60 mph	195	9.6	
103H	OGA-472	FCHS	420	8.8	
103I	OGA-472	60 mph	295	11.6	
104G	CI-2	FCCS	437	7.6	256A
107A	CI-2	60 mph	441	12.0	
107B	CI-2	FCHS	472	13.2	
107C	CI-2	60 mph	345	15.2	
107D	CI-2	FCHS	498	13.6	
107E	CI-2	60 mph	402	14.4	
107F	CI-2	FCHS	422	16.0	
107G	CI-2	60 mph	616	14.4	
107H	CI-2	FCCS	465	17.6	
107I	CI-2	60 mph	541	14.4	
108G	CI-2	FCHS	414	13.6	256B

TABLE 21
ENGINE DYNAMOMETER TEST

ENGINE TYPE: 350 CID Chevrolet
FUEL: Indolene O, 91 Octane

						GRAMS PER MILE PARTICULATE			
	Additive			Anderson	Glass	Anderson +	Glass Filter, 1 cfm		
Run #	Type	Conc.	Test Mode	Sampler	Filter	Glass	142 mm	47 mm	Run #
254A	none	-	FCCS	.1833	.1613	.3446	.1797	.0513	254A
254B	none	-	60 mph	.0149	.0026	.0175	.0162	.0041	254B
255A	OGA-472	1.87 g/gal	60 mph	.0099	.0116	.0215	.0195	.0050	255A
255B	OGA-472	1.87 g/gal	FCCS	.2933	.2200	.5133	.3399	.1332	255B
256A	CI-2	.9988 g/gal	FCCS	.1687	.1687	.3373	.1760	.1613	256A
256B	CI-2	.9988 g/gal	60 mph	.0185	.0270	.0465	.0291	.0110	256B

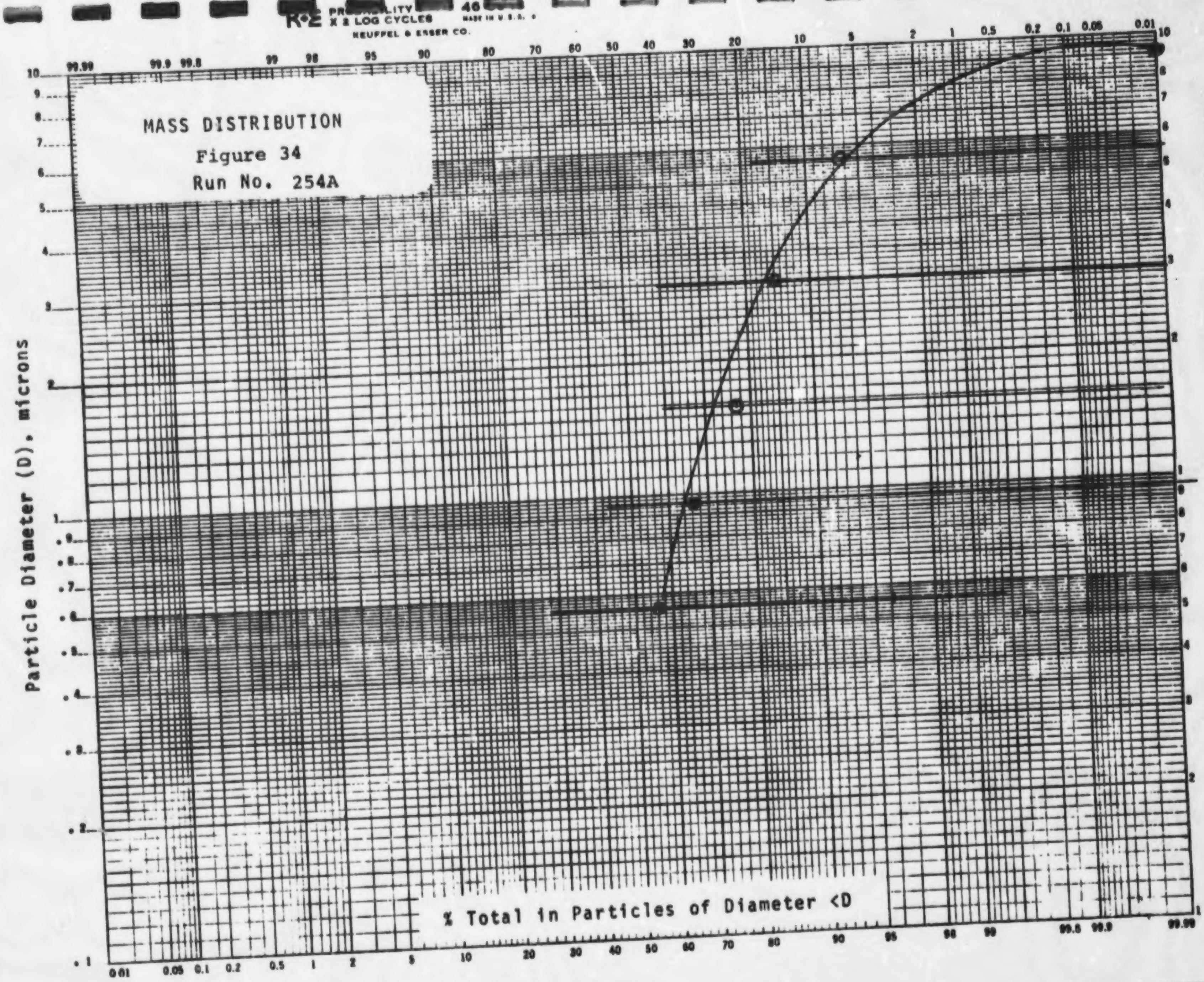
TABLE 21 Con't.
EXHAUST GAS ANALYSIS

	% by Volume				Parts per Million				Exhaust Condensate		
Run #	CO_2	O_2	N_2	CO	H.C.	NO_2	NO	NO_x-N_x	ppm HCHO	ppm NH_3	ppm HCHO in exhaust
254A	10.0	6.1	82.3	.64	130			726	453	10.4	
254B	9.9	6.9	82.3	.03	70			1100	263	15.6	
255A	10.0	6.8	82.2	.03	70			1400	226	6.8	
255B	10.0	6.2	82.2	.76	250			1027	251	7.2	
256A	9.9	6.5	82.3	.42	150			873	437	7.6	
256B	9.8	6.9	82.2	.08	100			1080	414	13.6	

TABLE 21 Con't.
ANALYSIS OF EXHAUST PARTICULATE

% on Millipore Filter

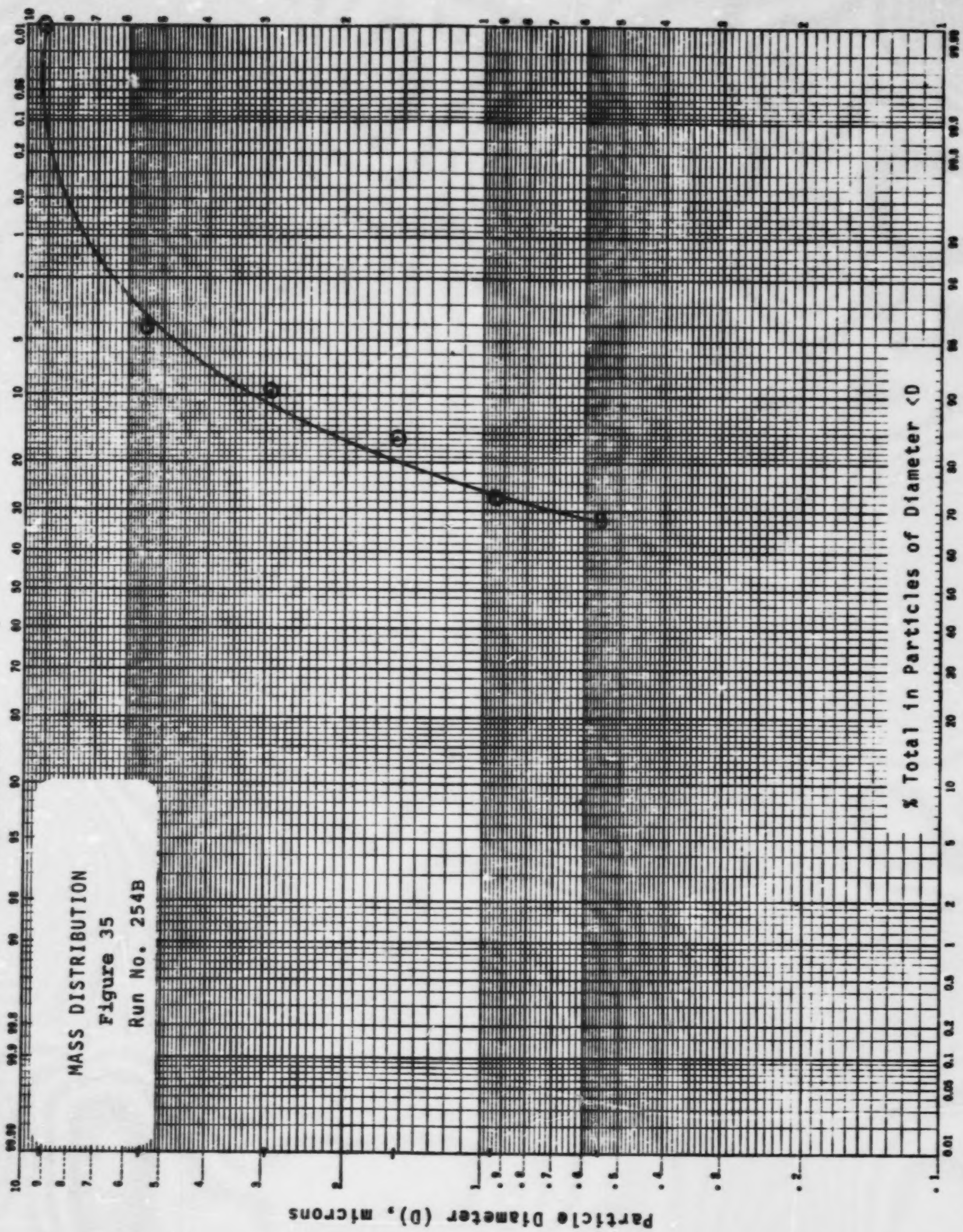
Run #	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	% C	% H	% N	benzene Solubles	ppm BAP
254A	.8	<.1	.3	.4	2.6	.7	.4	<.1	<.3	1.7	<.1	1.2	19.37	5.5	4.4		420
254B	.5	<.1	.2	.2	2.6	.6	.03	<.1	<.3	1.0	<.1	1.8	18.74	8.9	3.5		50
255A	.6	<.1	.3	.3	3.0	.7	.02	<.1	<.3	1.0	<.1	1.5	15.74	6.1	3.7		82
255B	.6	<.1	.1	.1	1.1	.3	.05	<.1	<.1	0.4	<.1	0.2	11.78	6.5	3.2		2400
256A	.2	<.1	.1	<.1	1.5	.3	6.0	<.1	<.1	0.7	<.1	0.3	12.28	4.3	2.8		795
256B	.1	<.1	.06	<.1	.7	.1	4.2	<.1	<.1	0.8	<.1	<.3	24.30	9.9	4.2		160



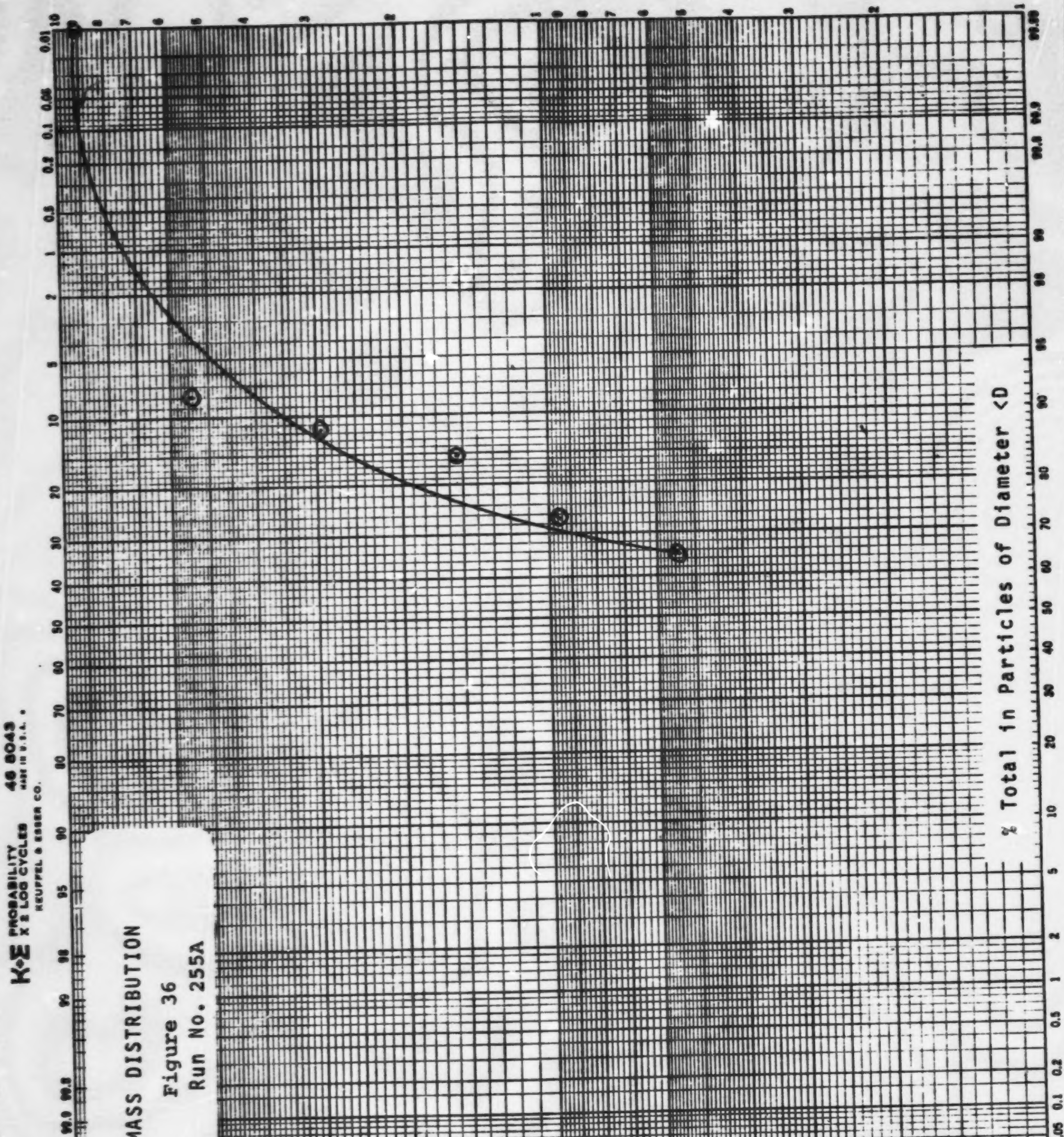
MASS DISTRIBUTION

Figure 34

Run No. 254A



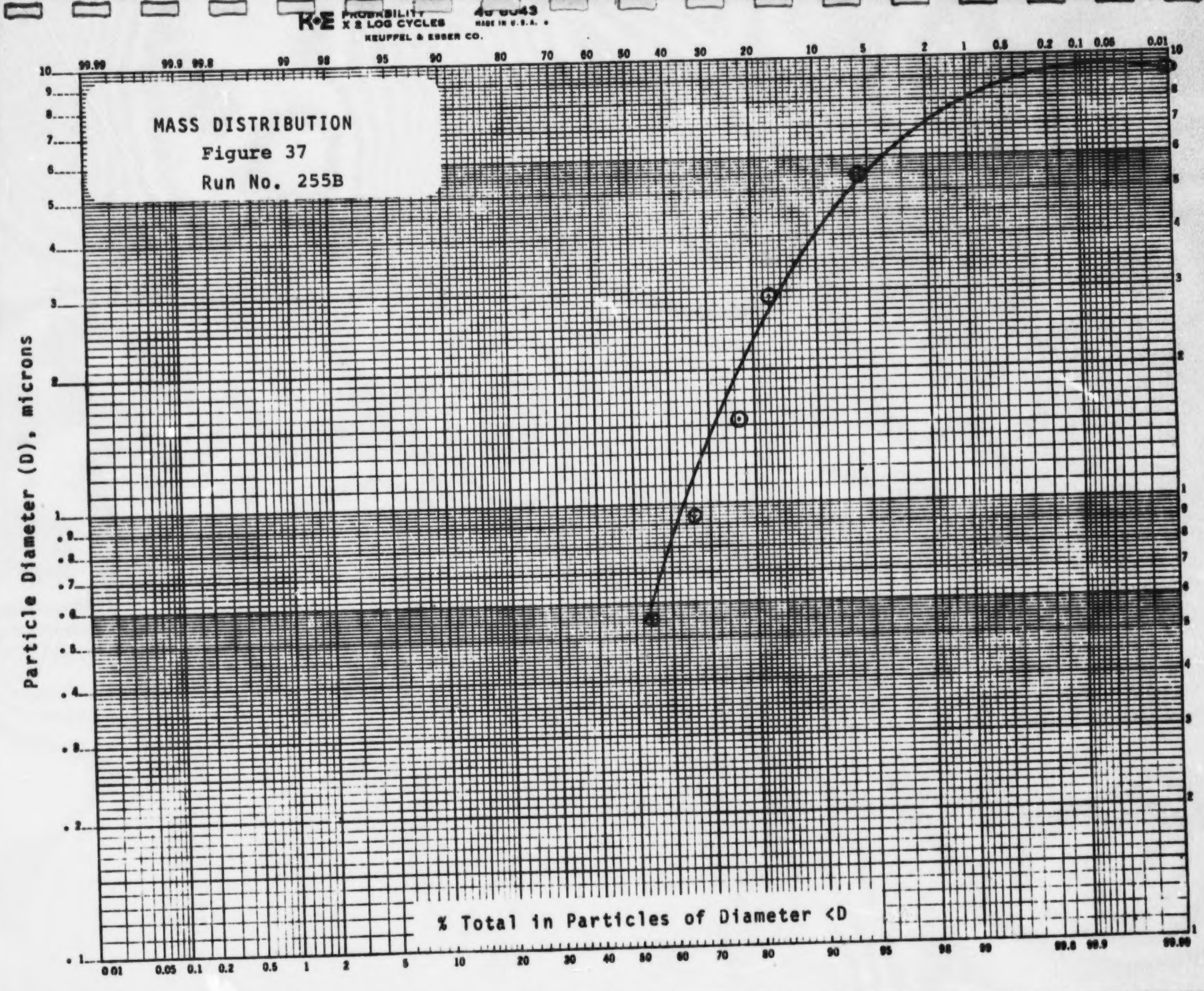
MASS DISTRIBUTION
Figure 35
Run No. 254B



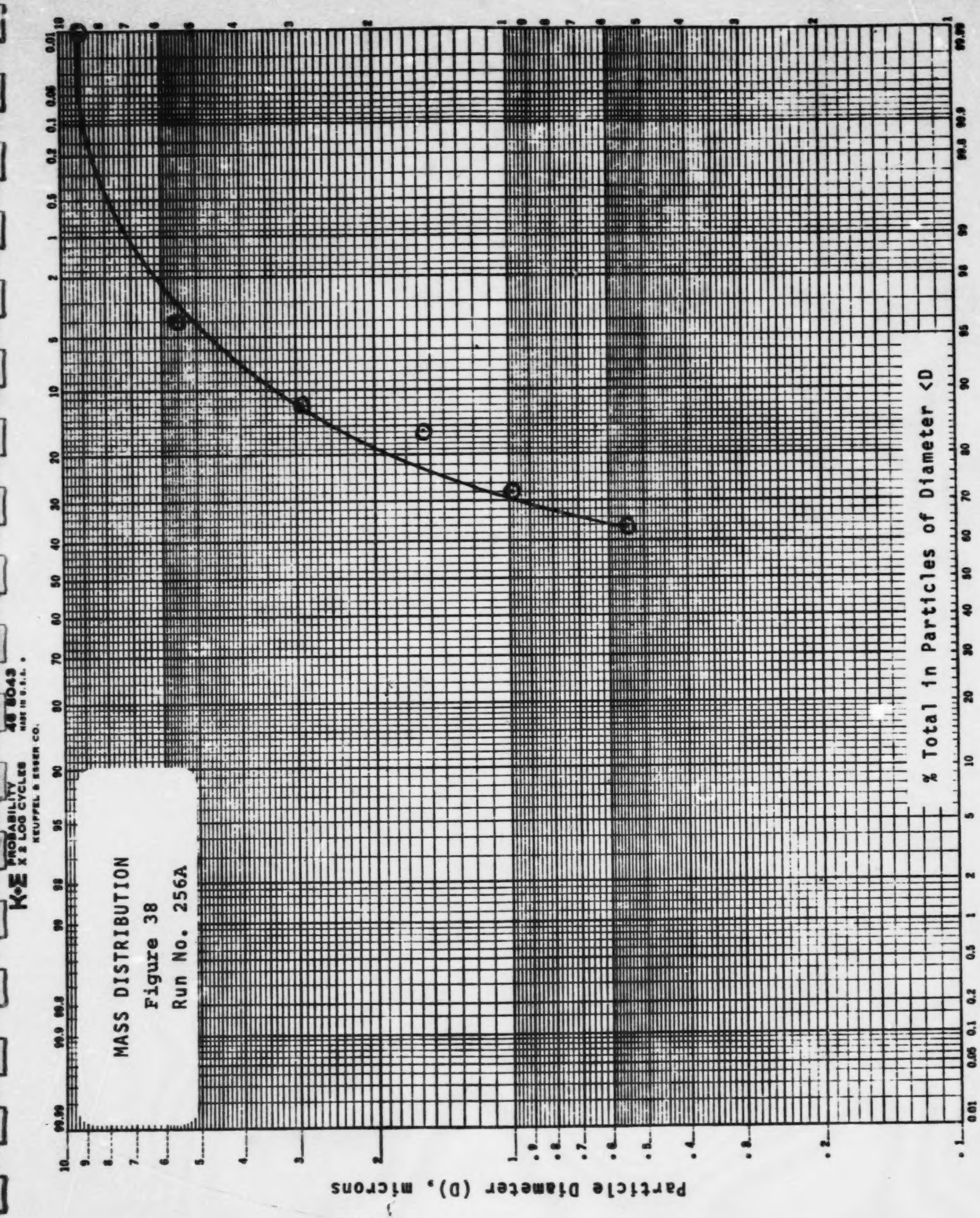
MASS DISTRIBUTION

Figure 36

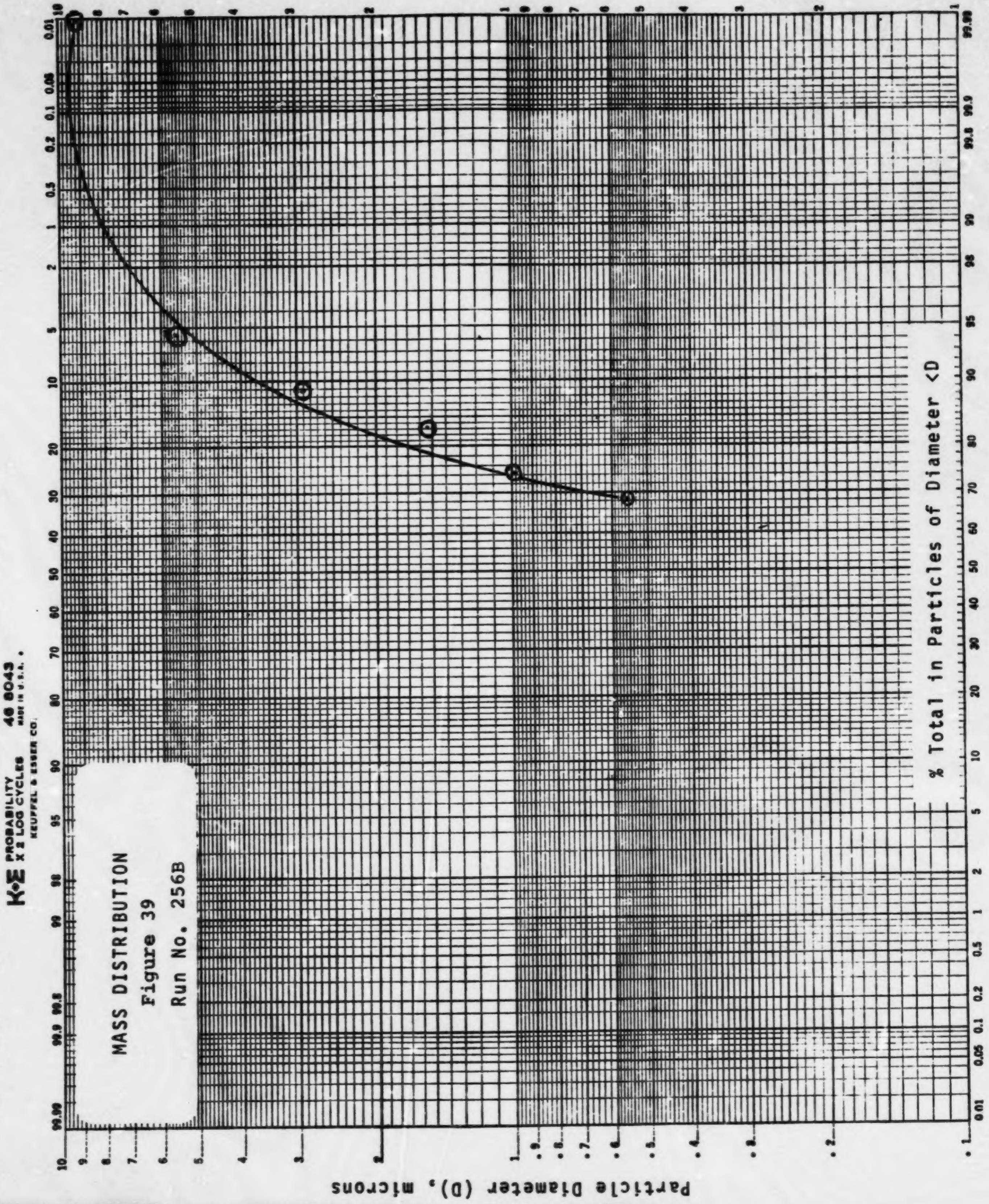
Run No. 255A



MASS DISTRIBUTION
Figure 37
Run No. 255B

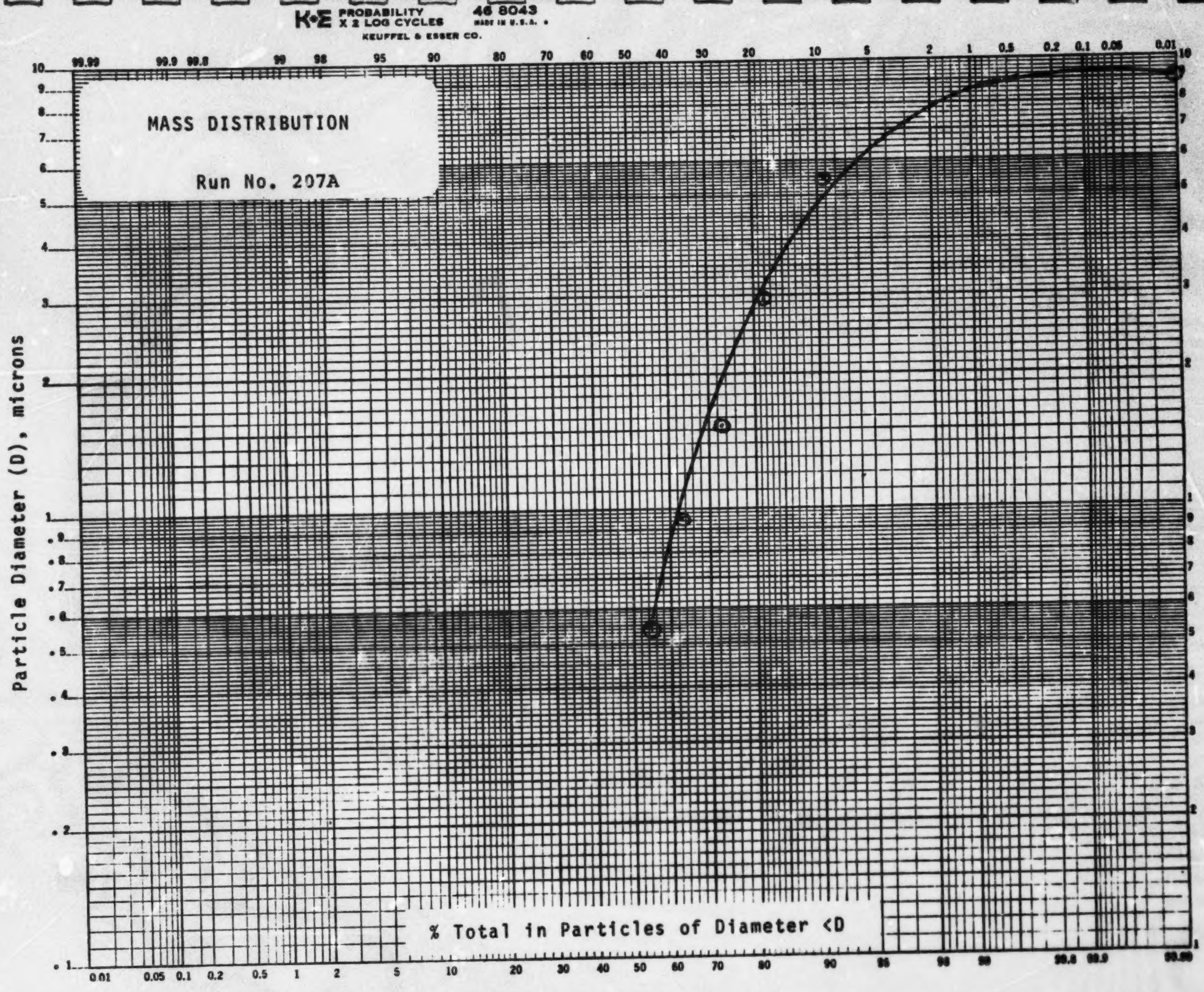


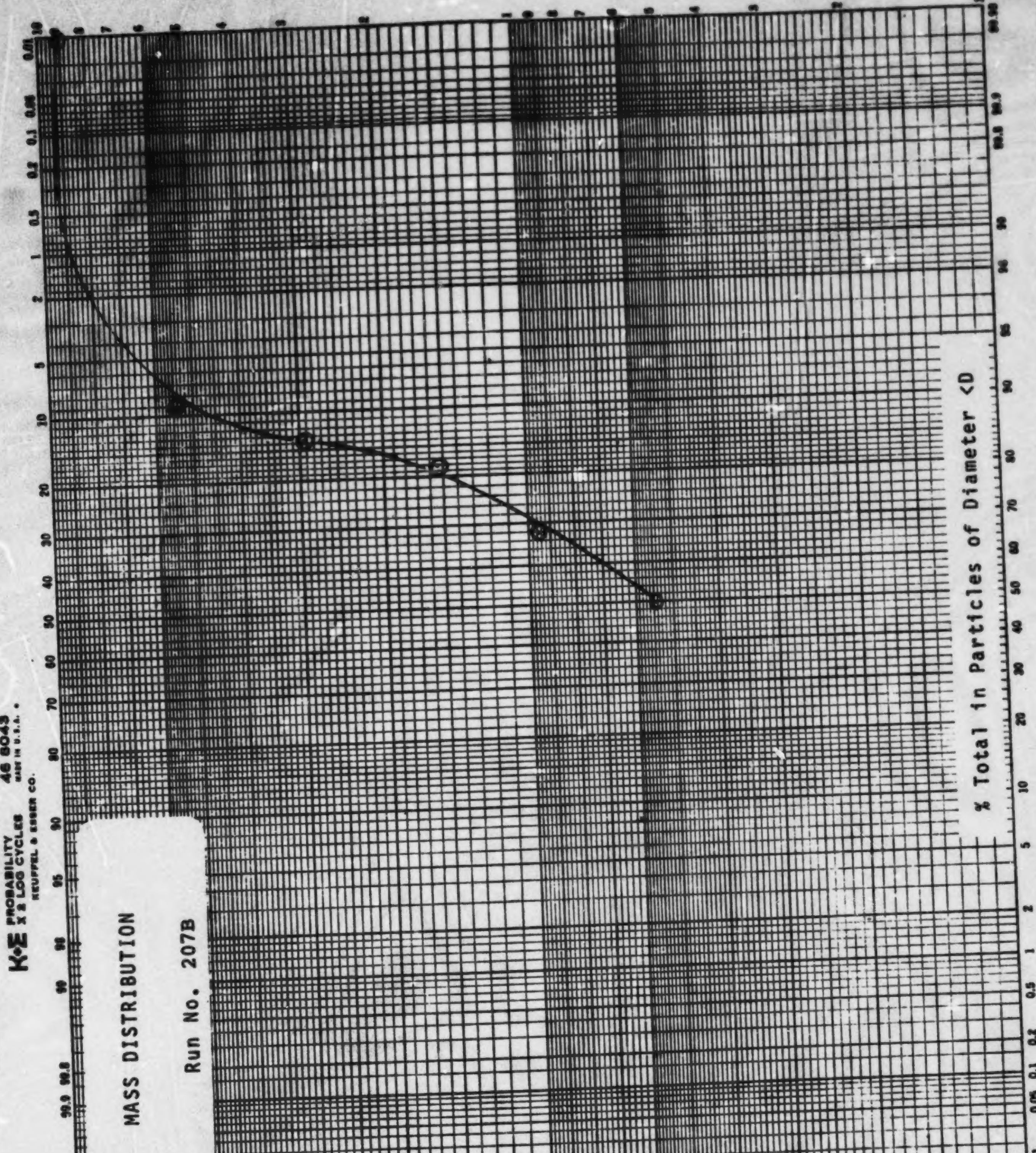
MASS DISTRIBUTION
Figure 38
Run No. 256A



MASS DISTRIBUTION
Figure 39
Run No. 256B

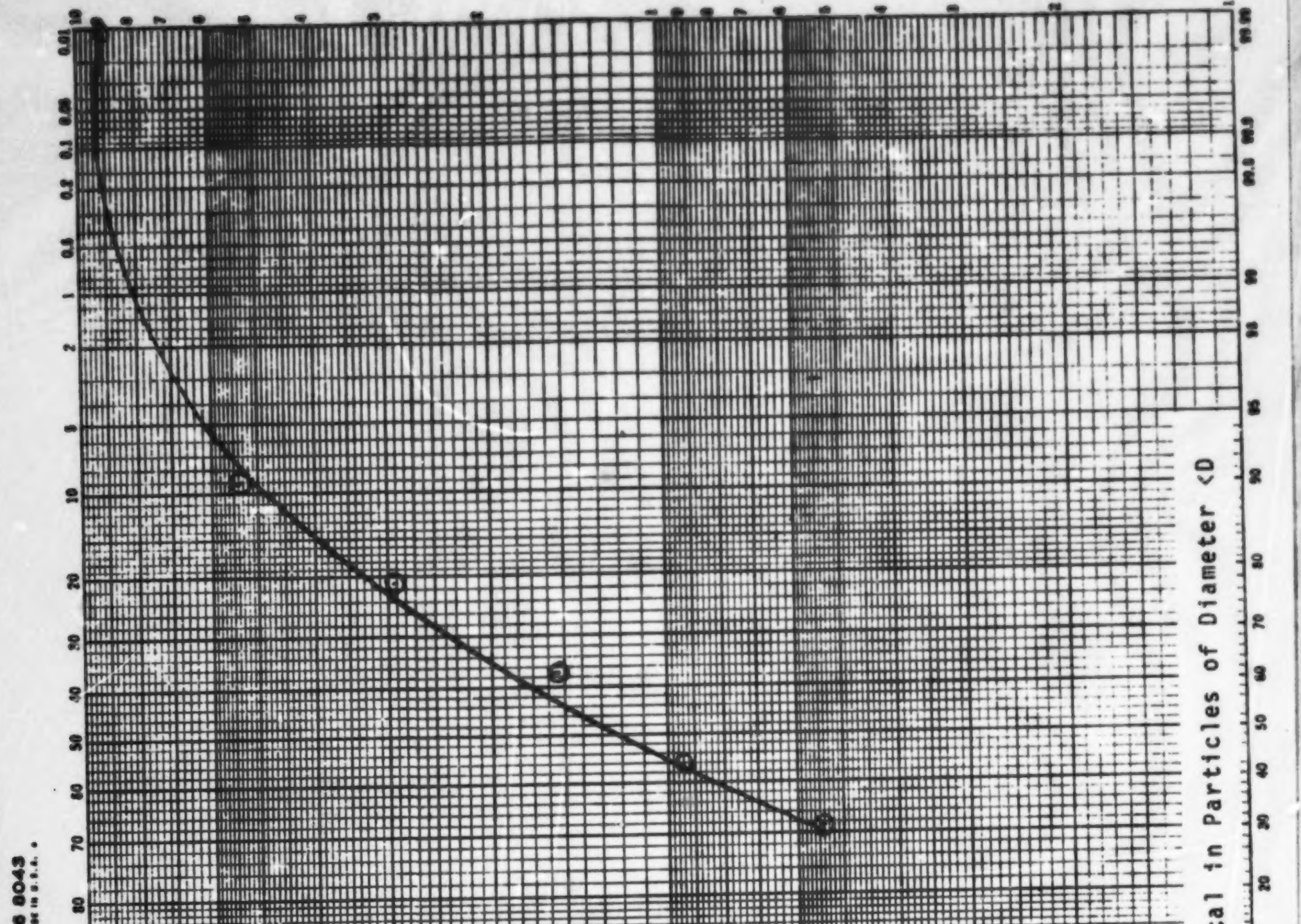
APPENDIX A

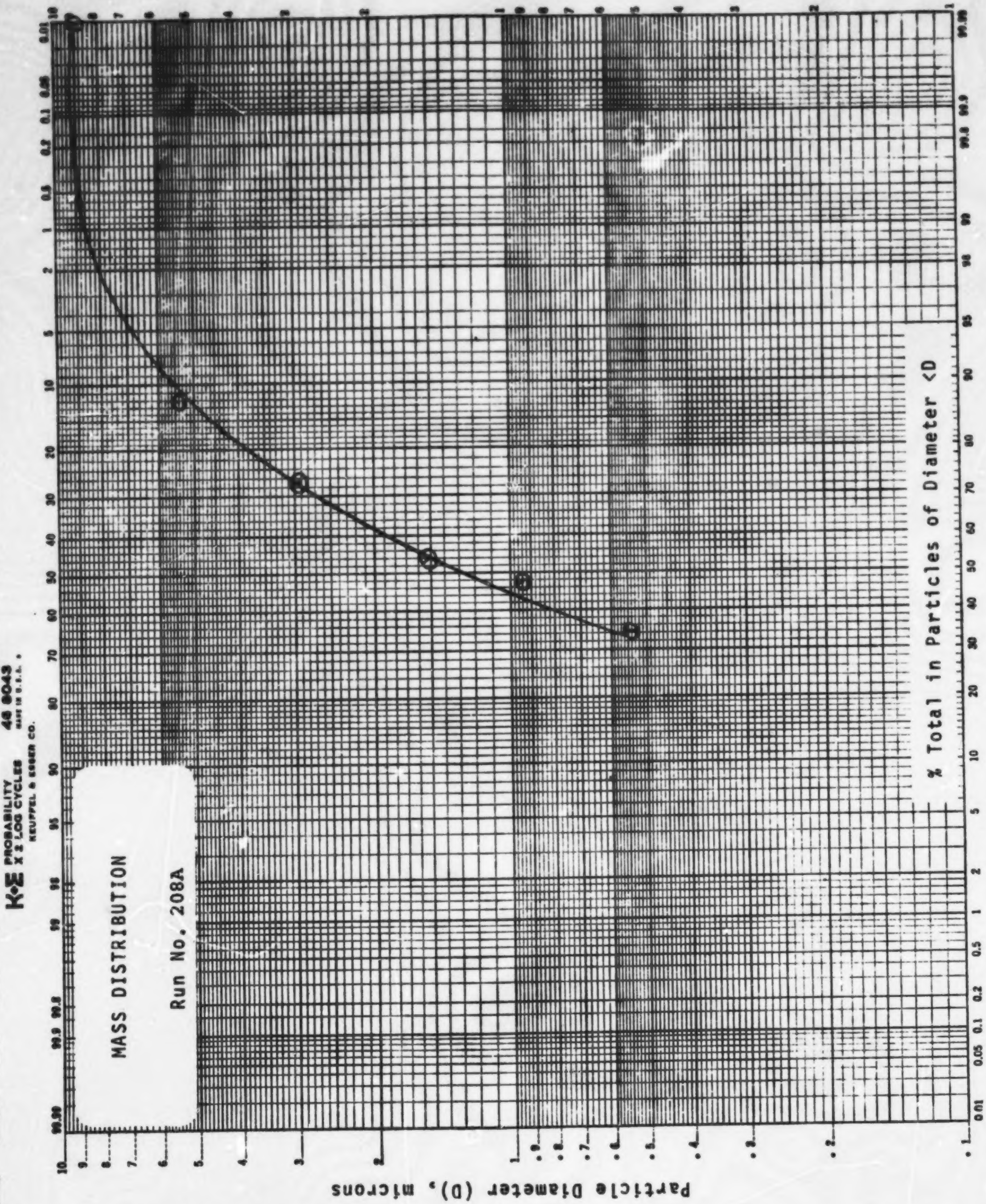

K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 207A
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99



MASS DISTRIBUTION

Run No. 207B


K+E PROBABILITY X 2 LOG CYCLES 46 8043 KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 207C
Particle Diameter (D), microns
% Total in Particles of Diameter <D


MASS DISTRIBUTION
Run No. 208A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
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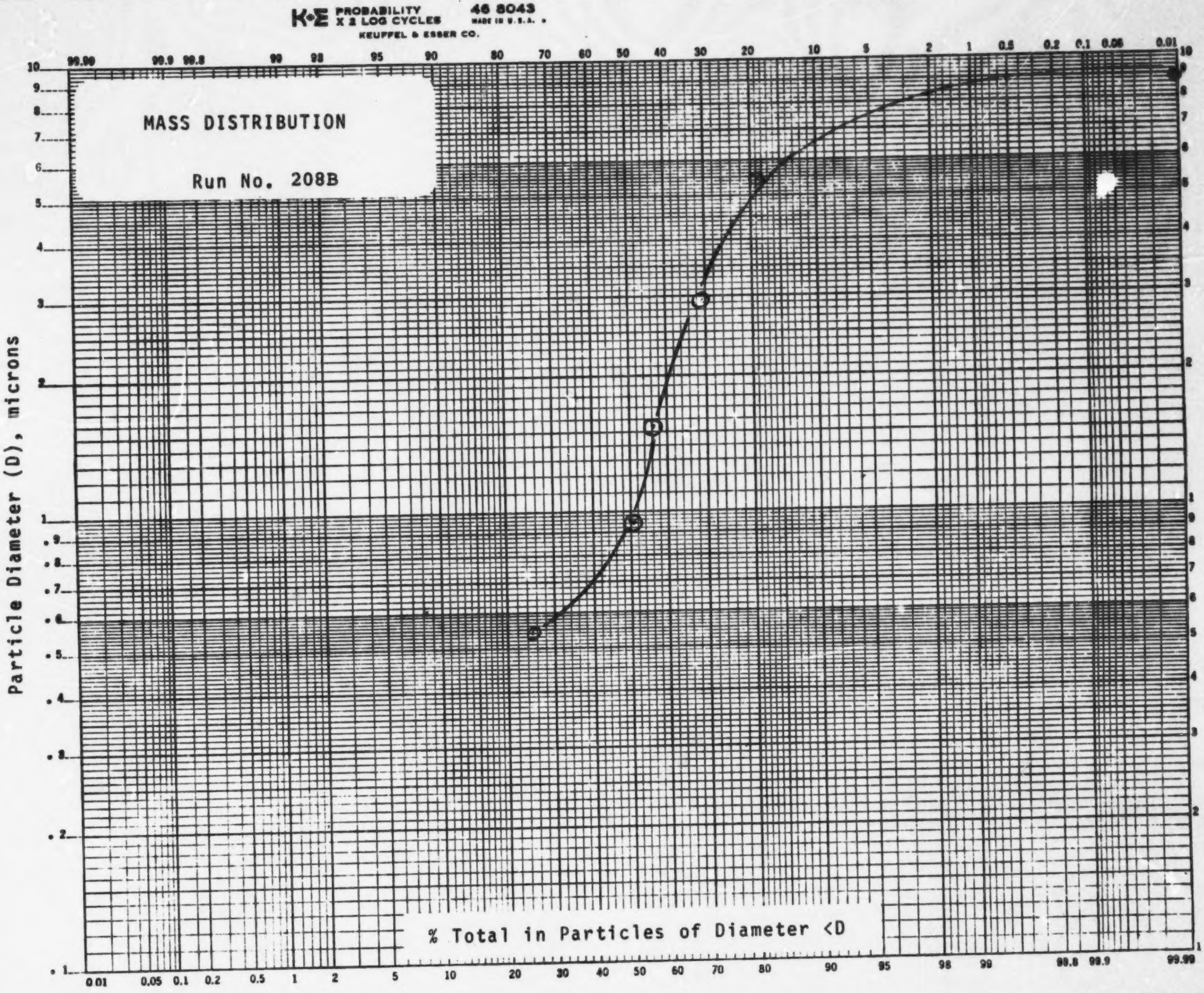
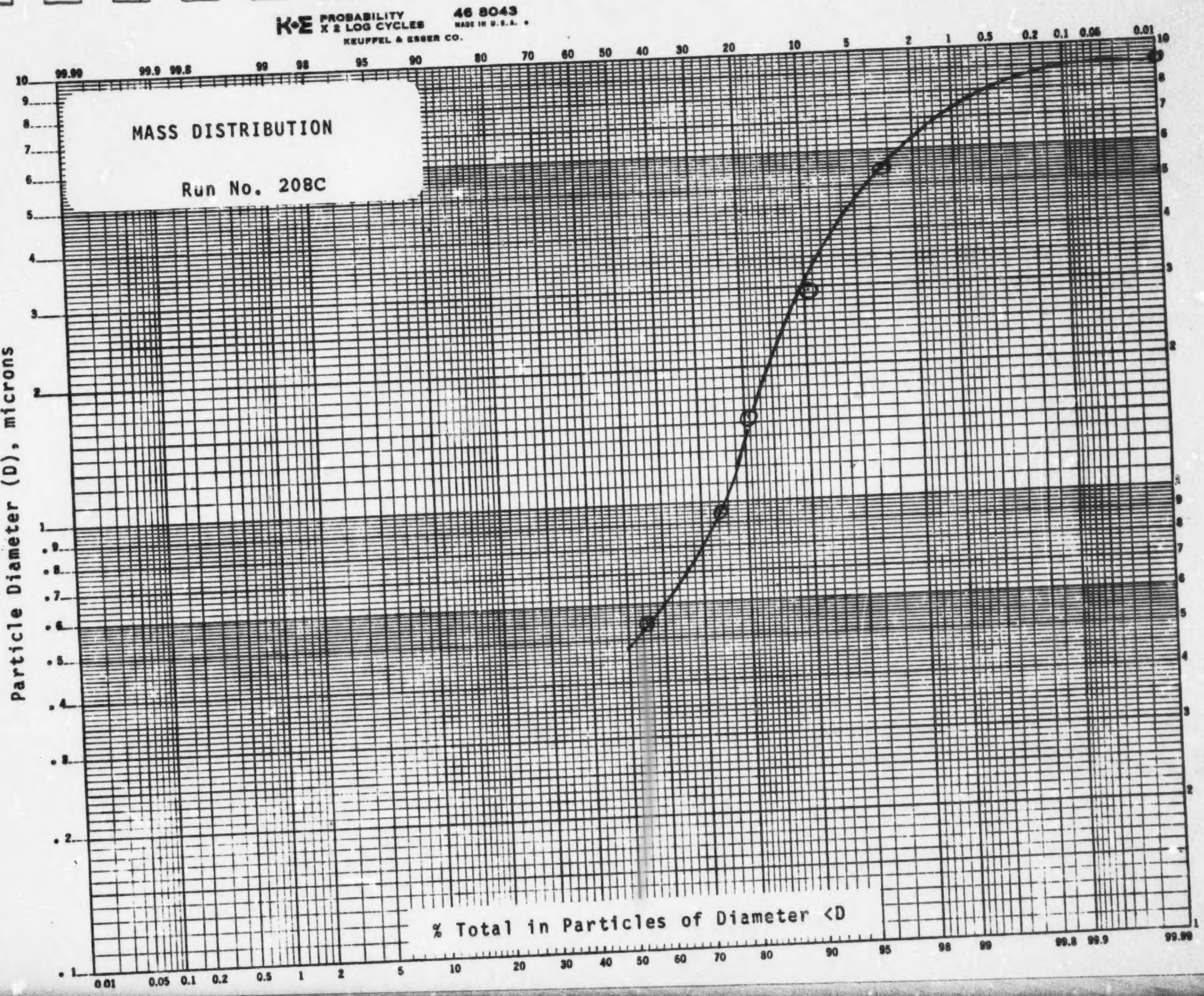
50
60
70
80
90
95
98
99
99.8
99.9
99.99


K+E PROBABILITY X 2 LOG CYCLES
46 8043 MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 208B
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99


K+E PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
46 8043
MADE IN U.S.A.
MASS DISTRIBUTION
Run No. 208C
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
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.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
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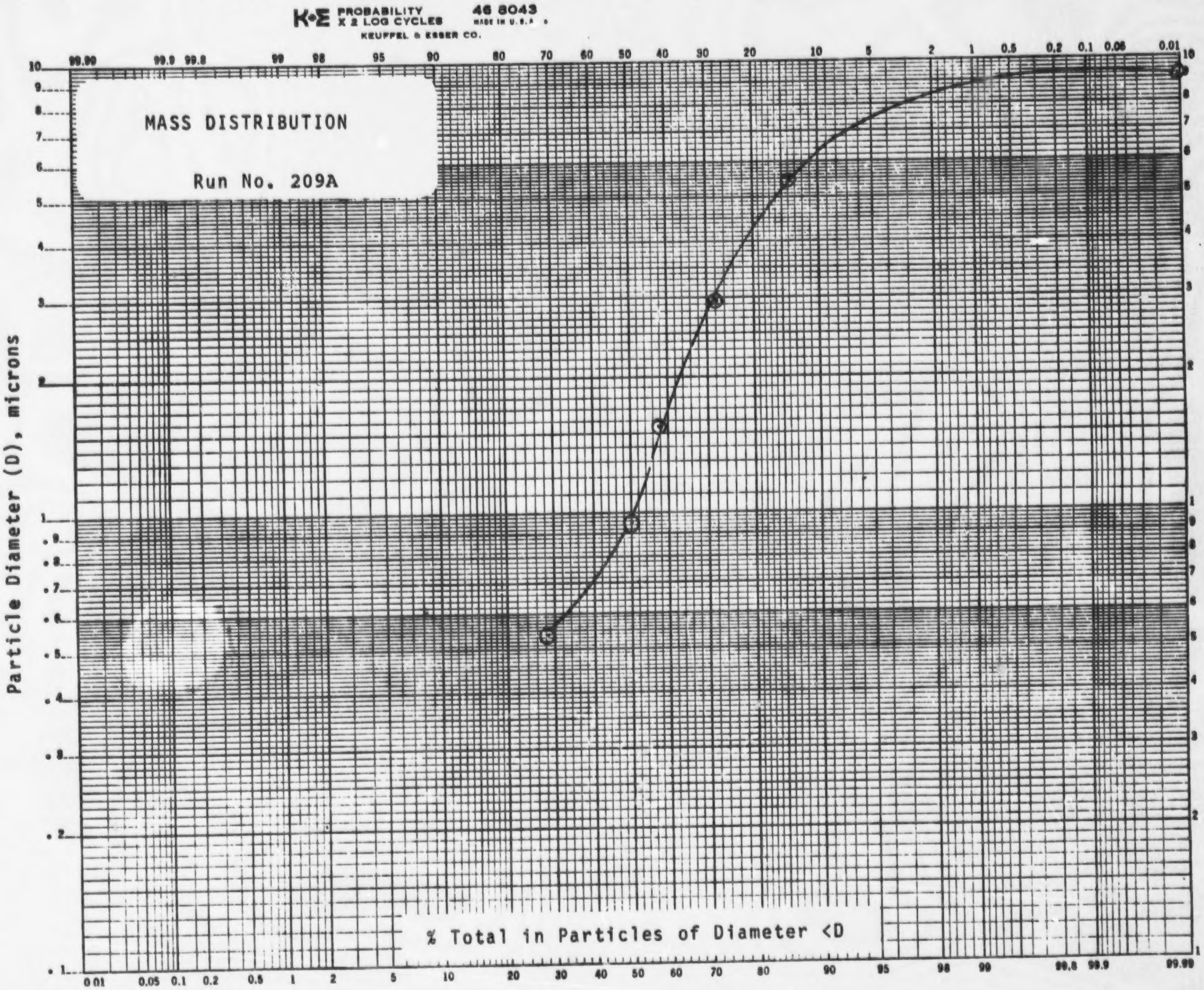
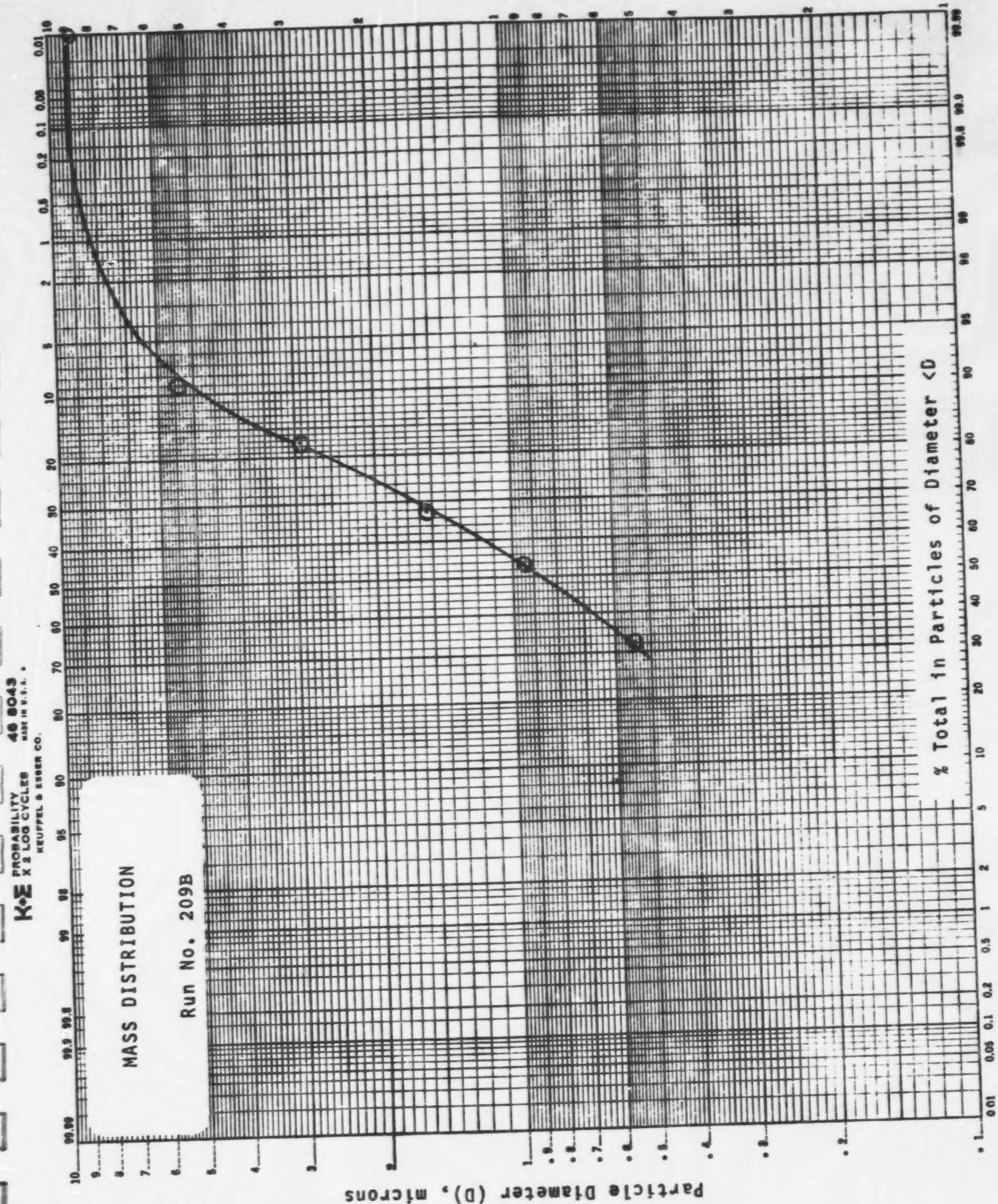
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99



MASS DISTRIBUTION

Run No. 209A


MASS DISTRIBUTION
Run No. 209B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
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9
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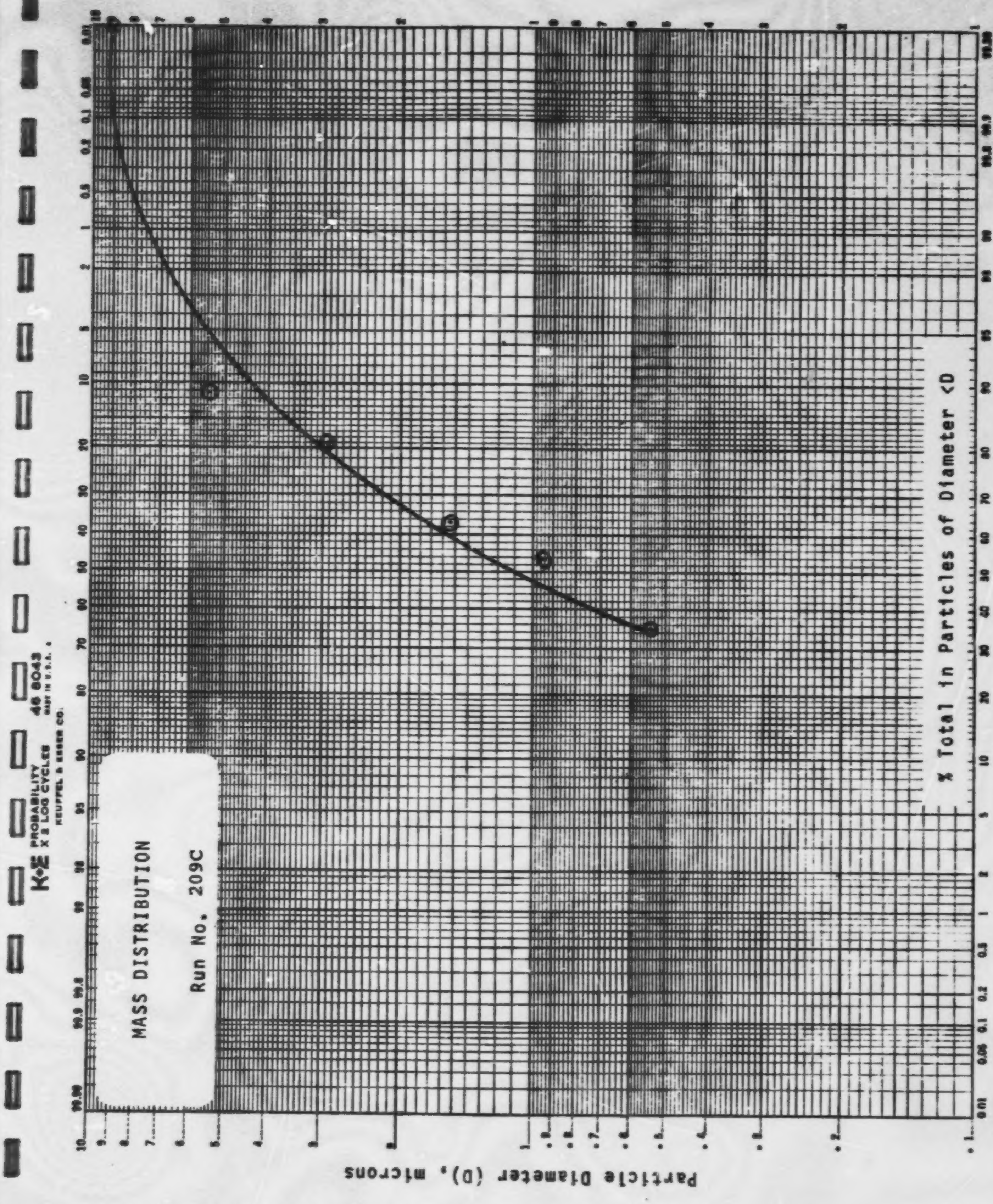
.2
.1


MASS DISTRIBUTION
Run No. 209C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
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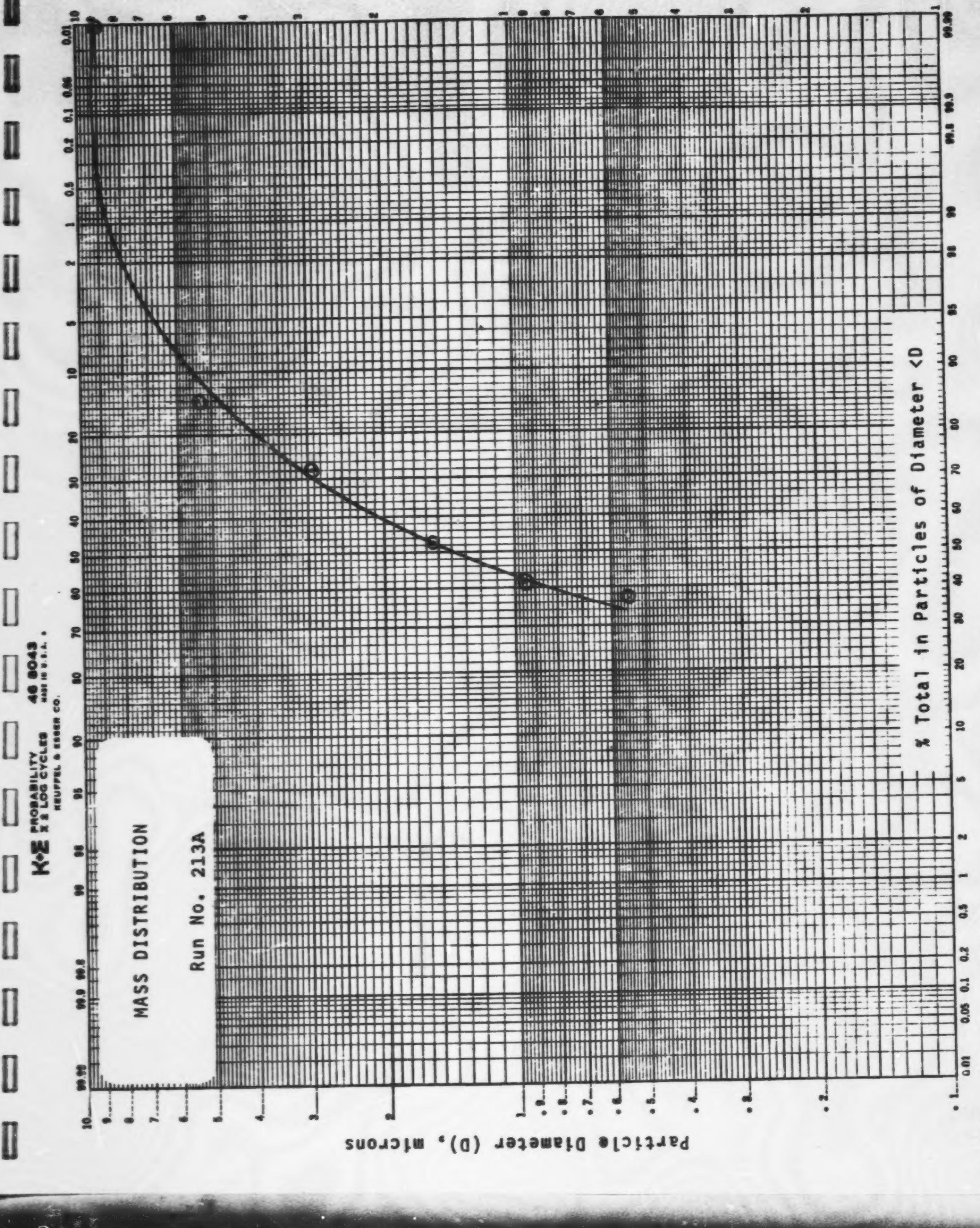
.1


MASS DISTRIBUTION
Run No. 213A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 3 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
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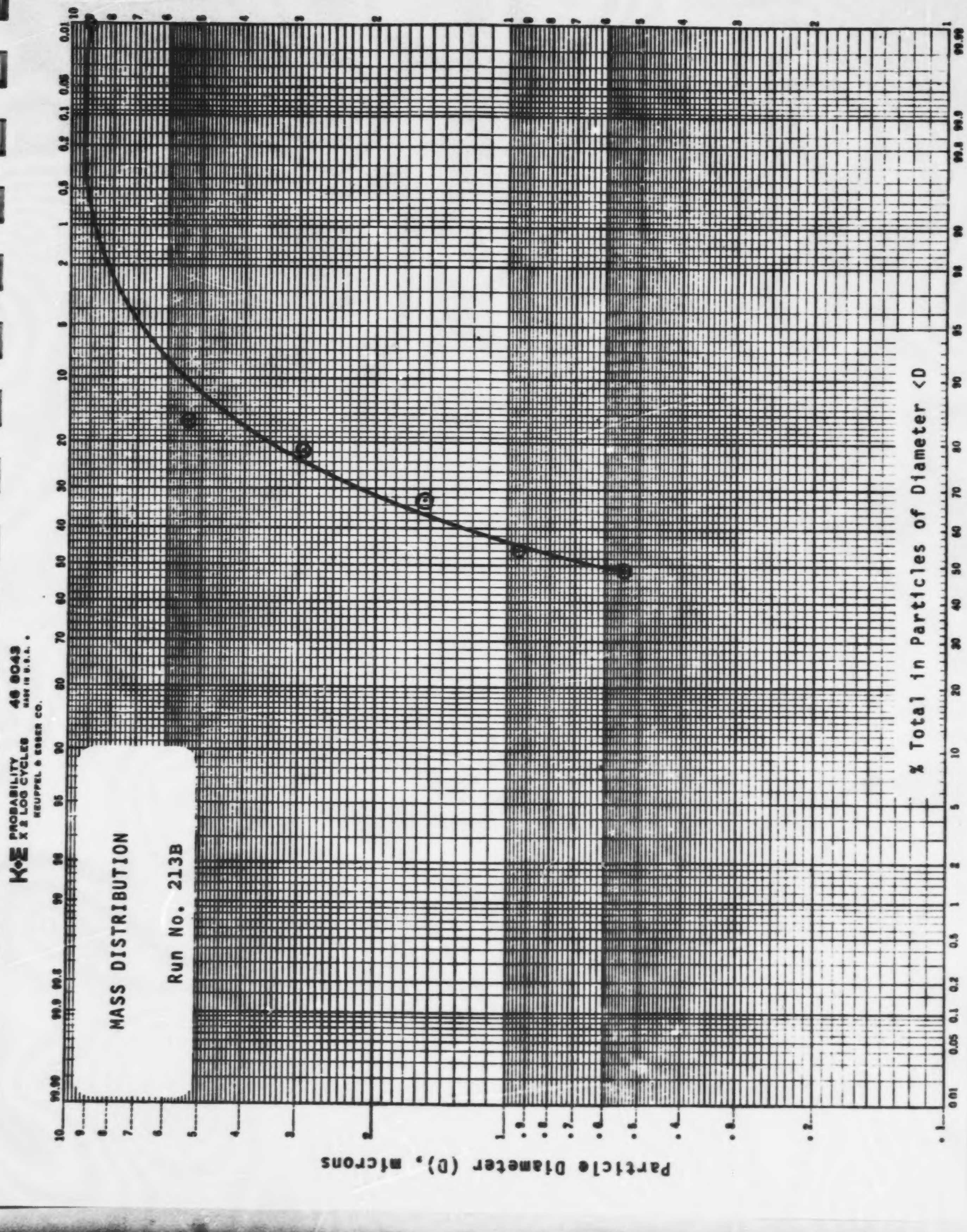
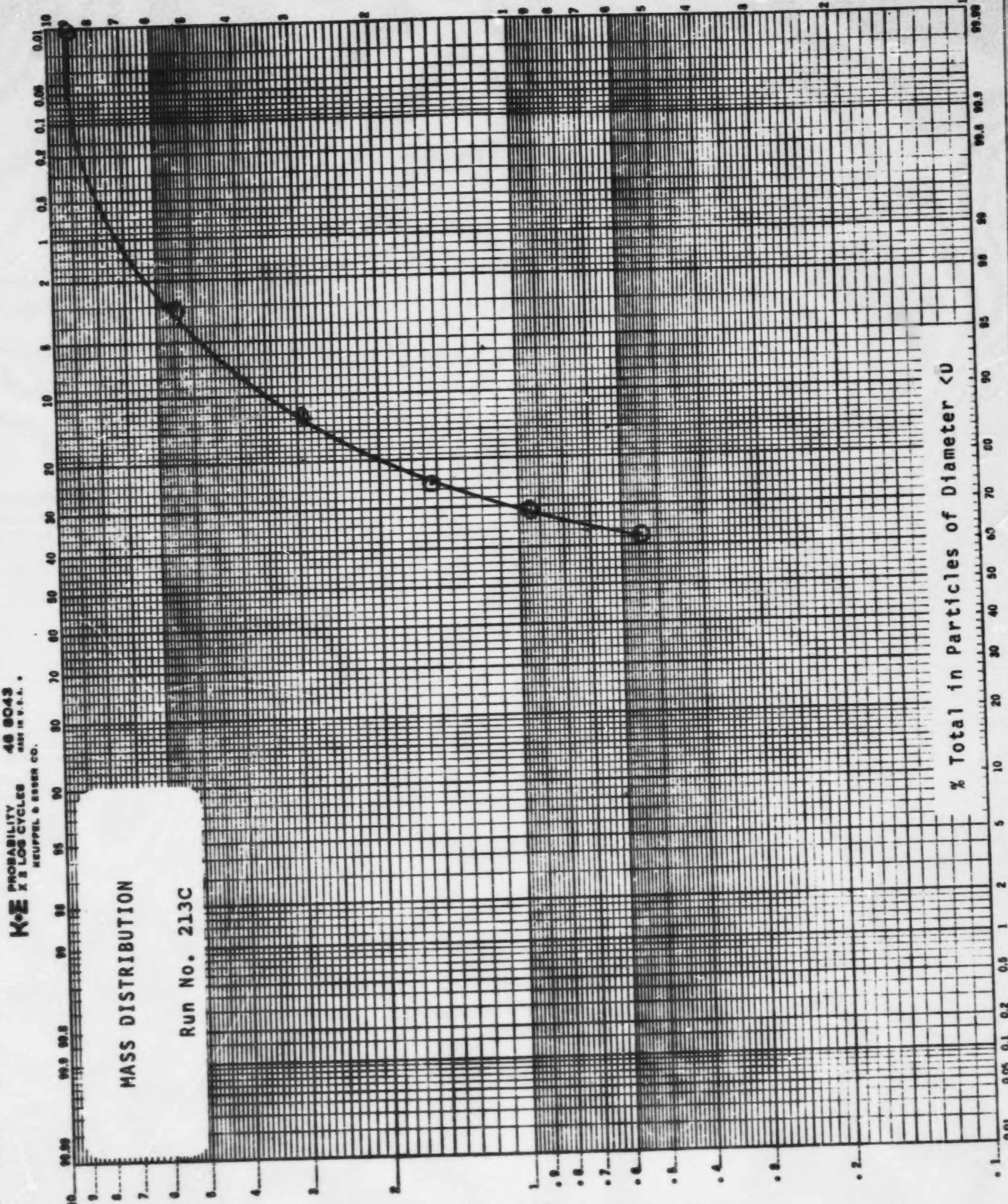
.8
.7
.6
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 213B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
10
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
MADE IN U.S.A.


MASS DISTRIBUTION
Run No. 213C
Particle Diameter (D), microns
% Total in Particles of Diameter <D
K+E PROBABILITY X 3 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
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5
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20
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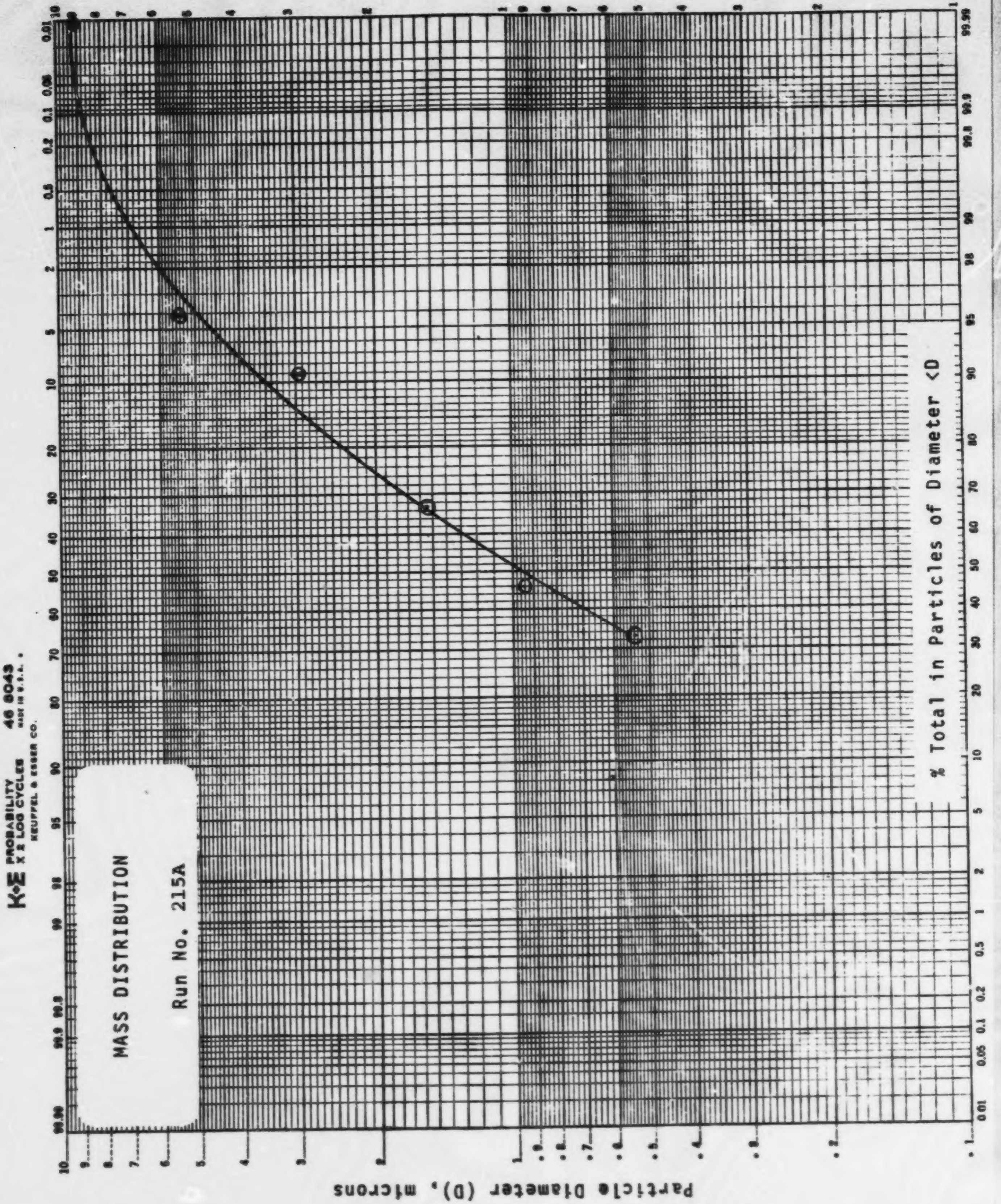
60
70
80
90
95
98
99
99.8
99.9
99.99


MASS DISTRIBUTION
Run No. 215A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
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4
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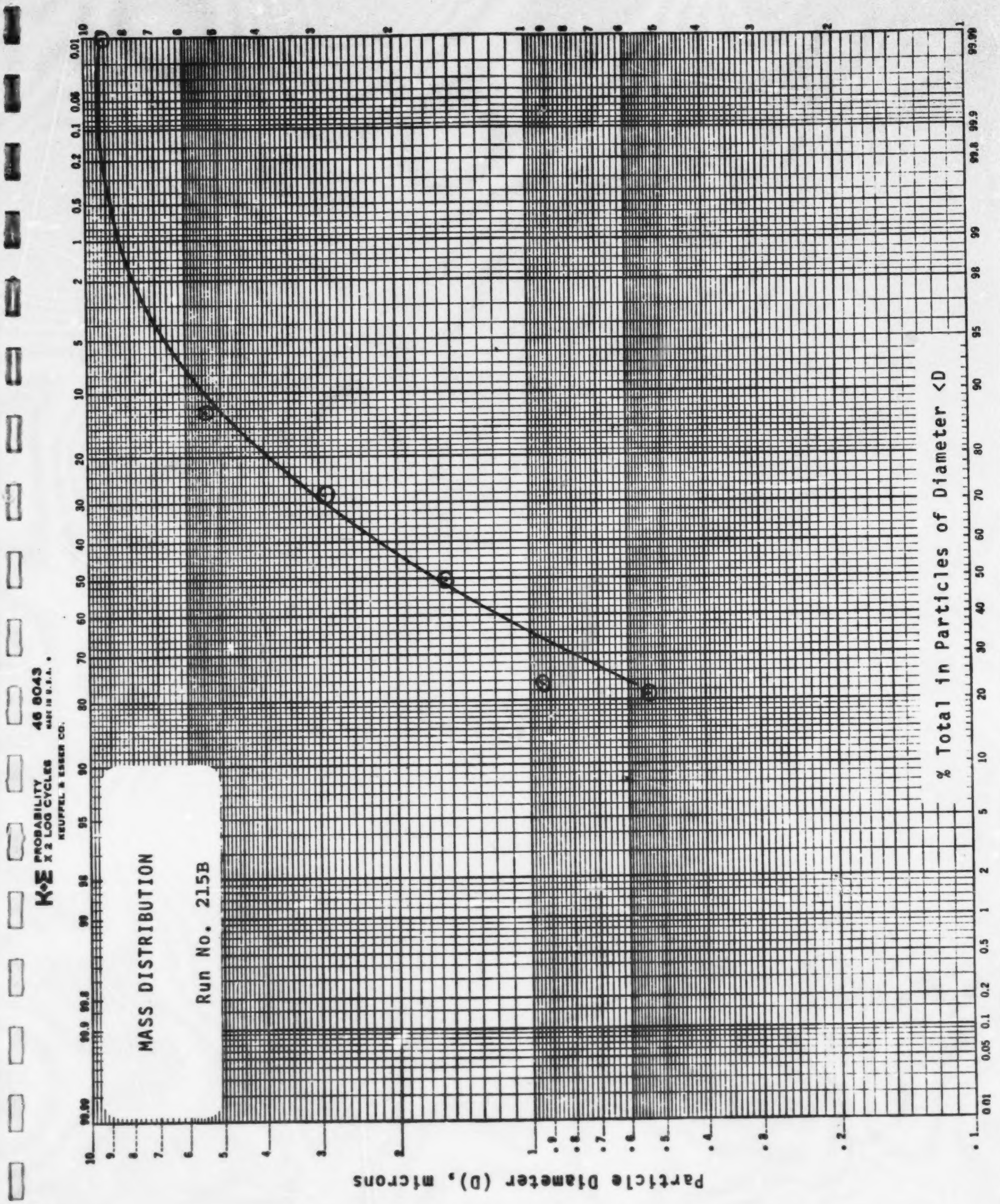
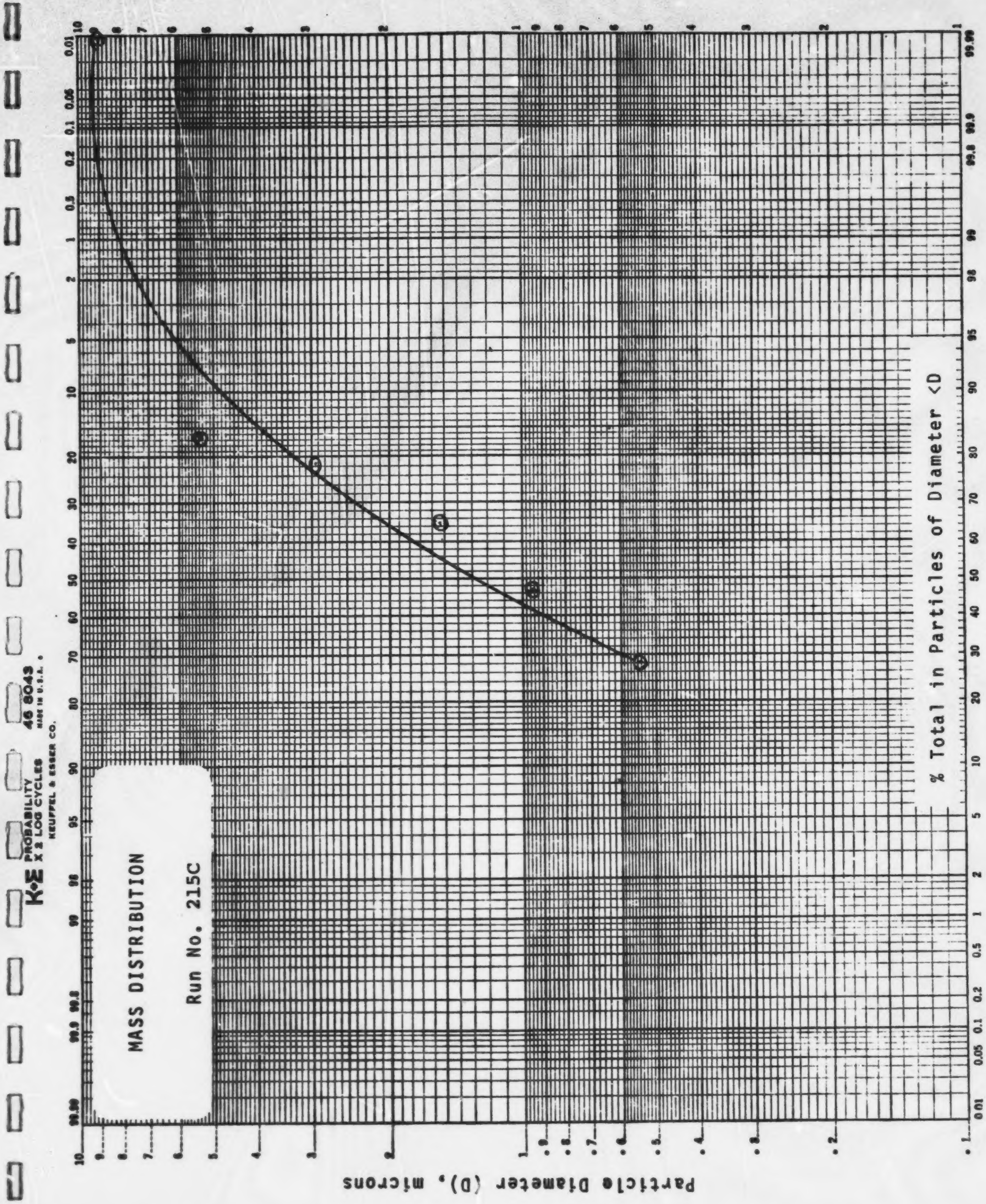
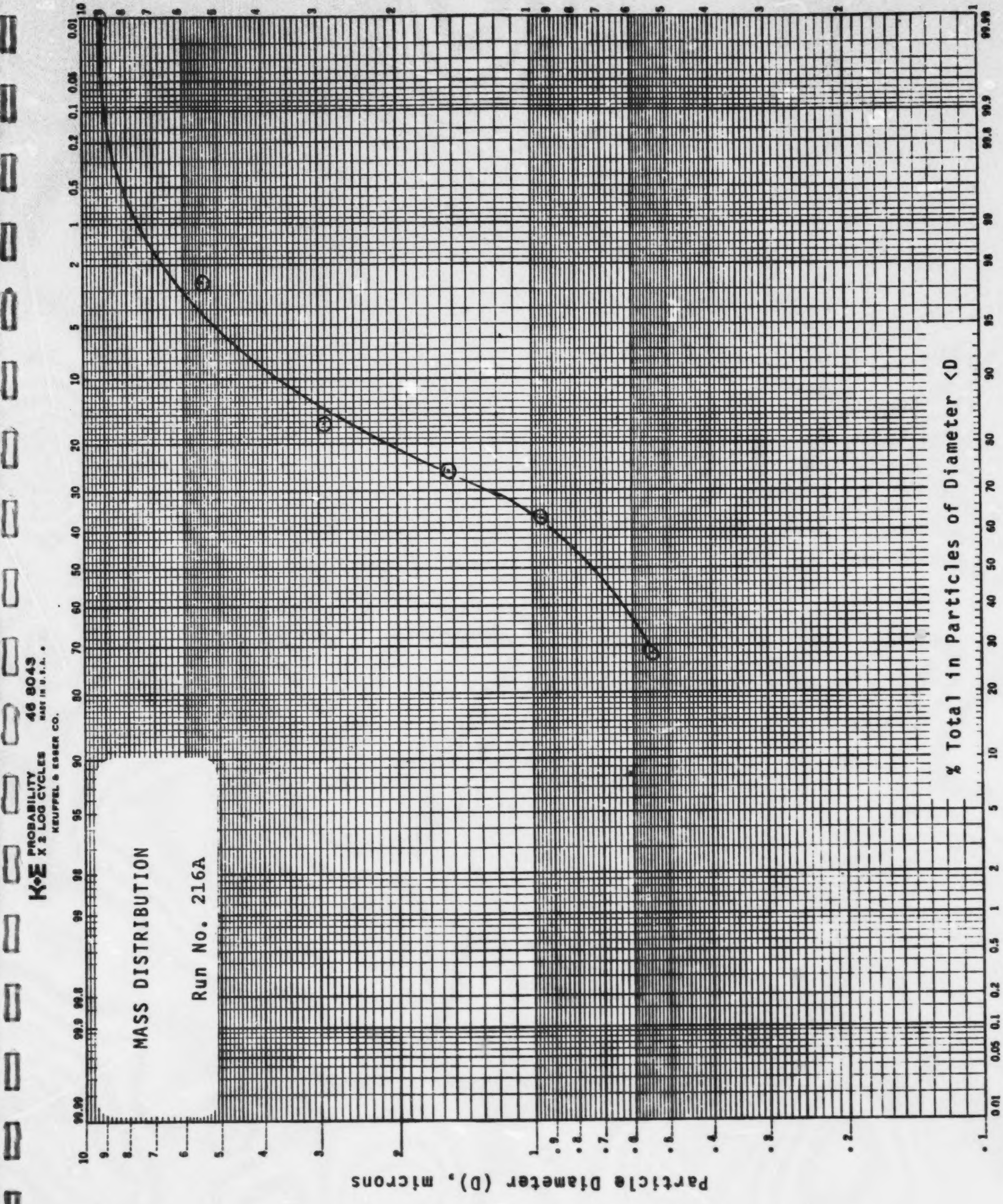
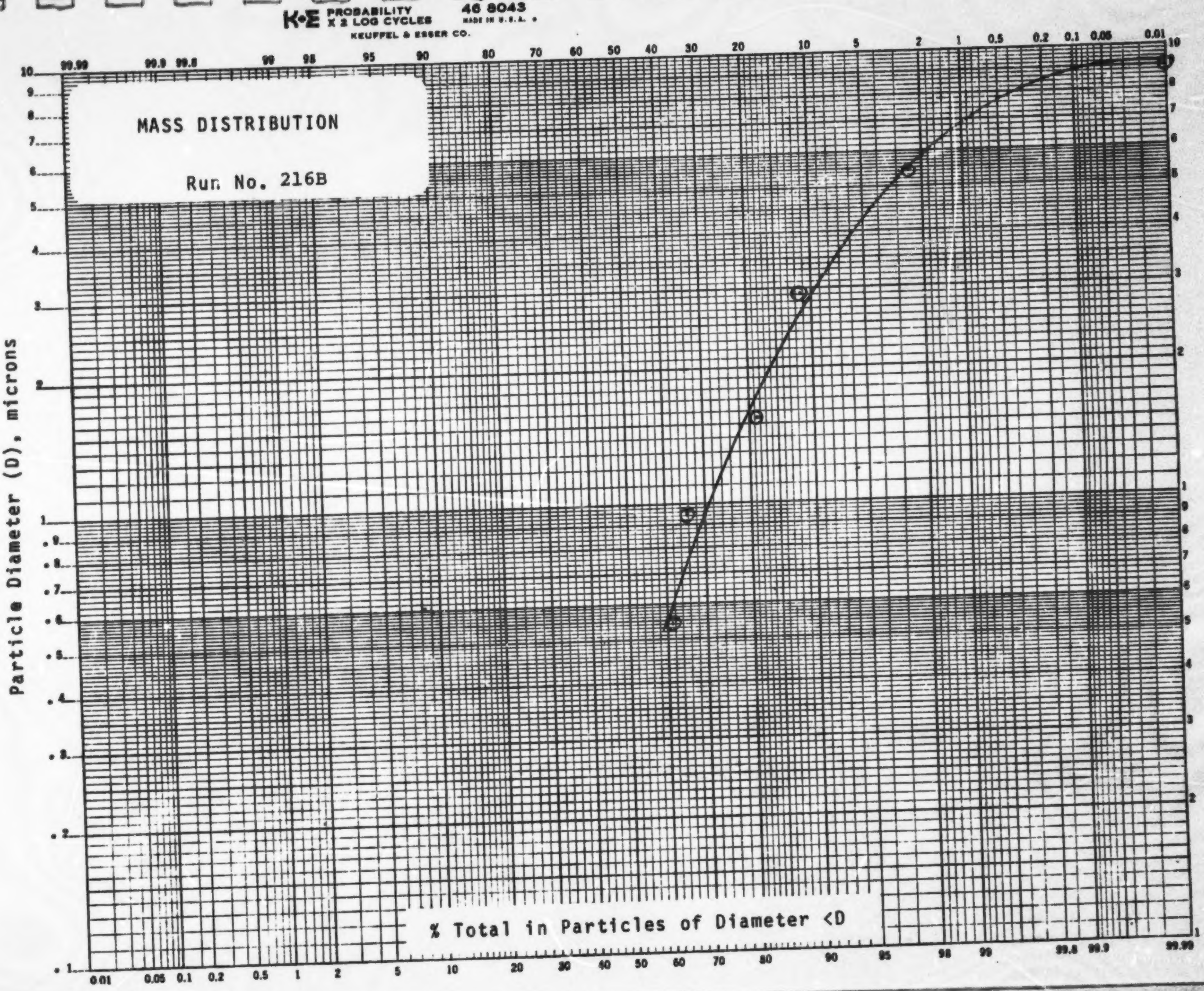
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 215B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

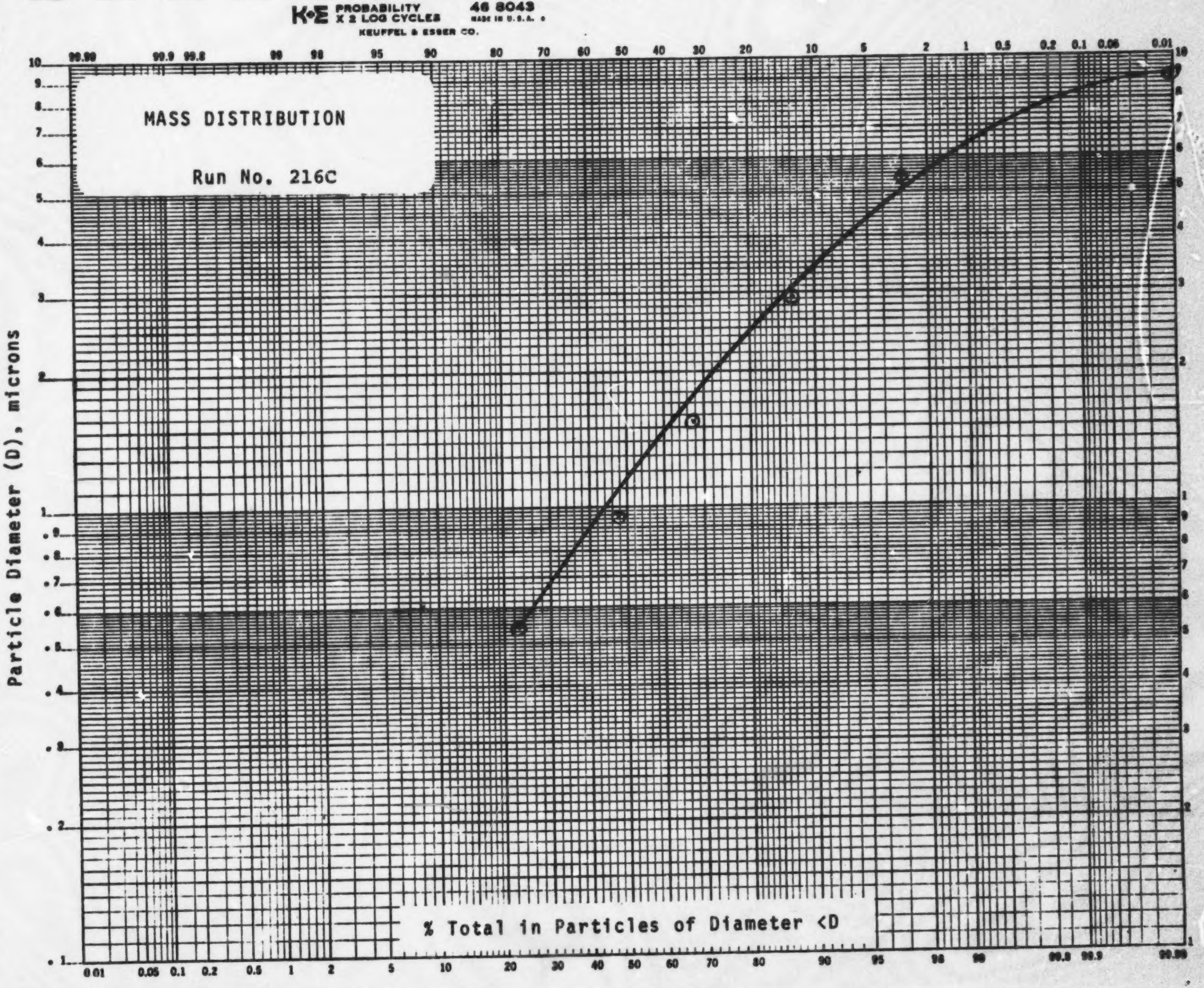

MASS DISTRIBUTION
Run No. 215C
Particle Diameter (D), microns
% Total in Particles of Diameter <D
K+E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

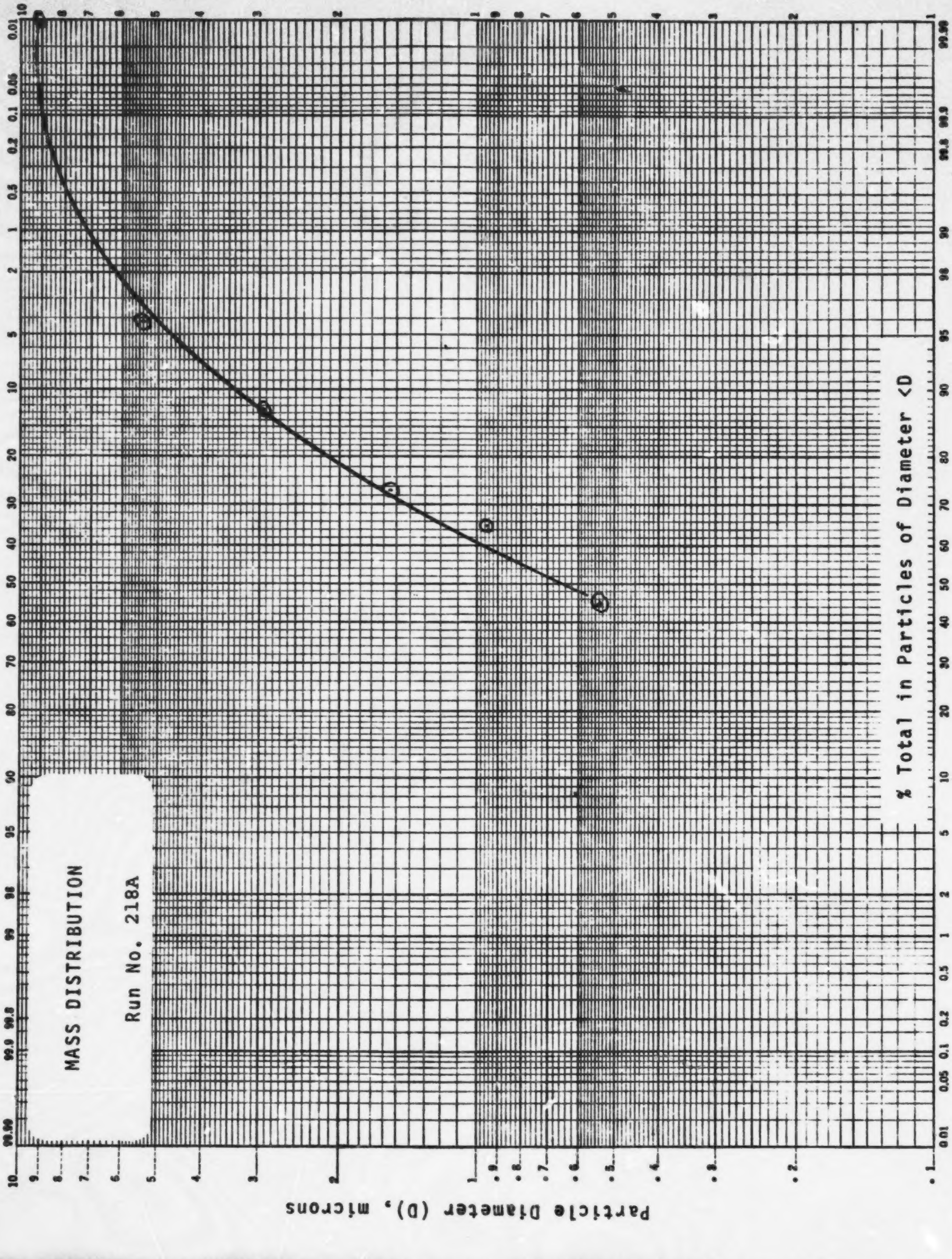

MASS DISTRIBUTION
Run No. 216A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
K•E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.

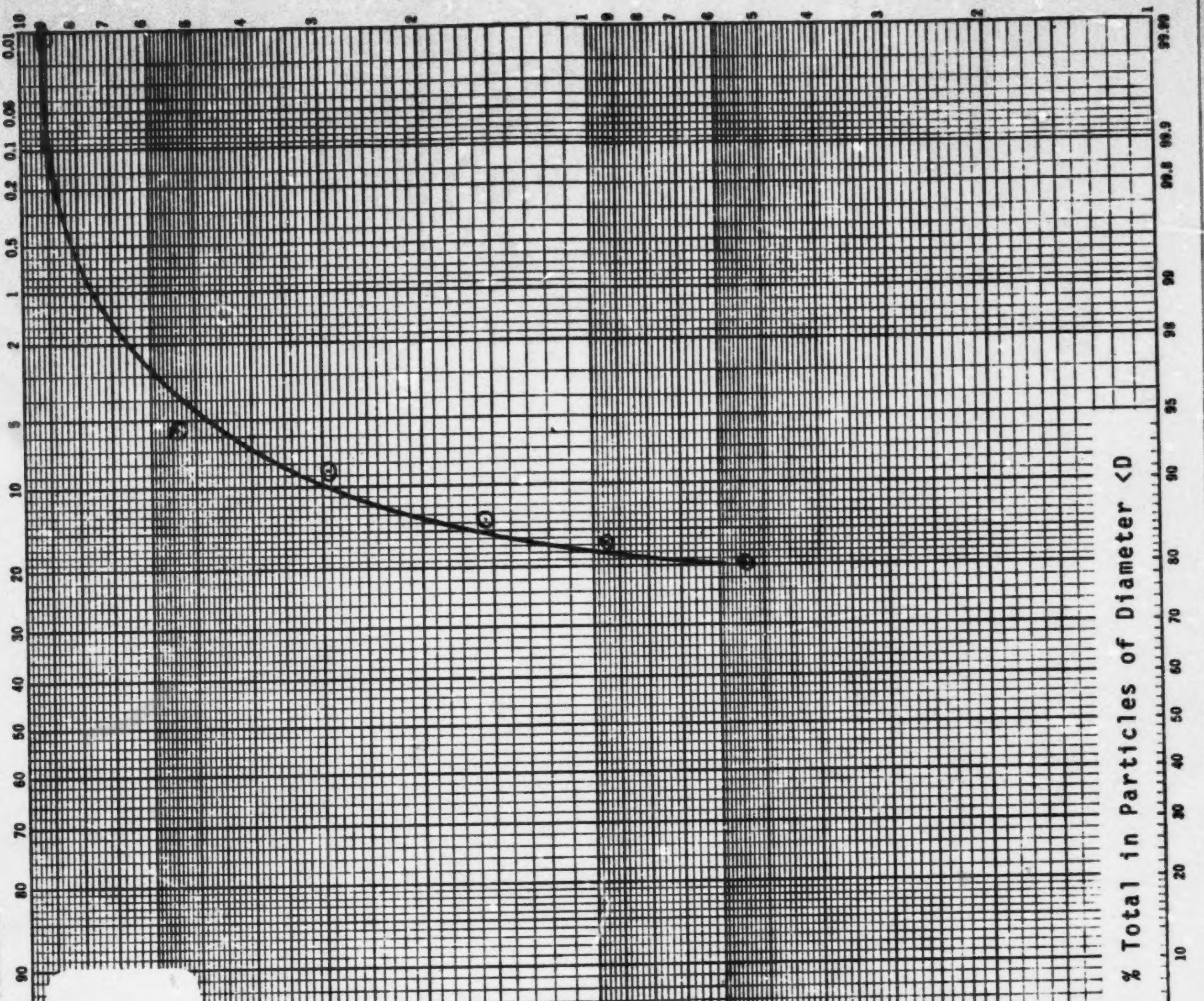


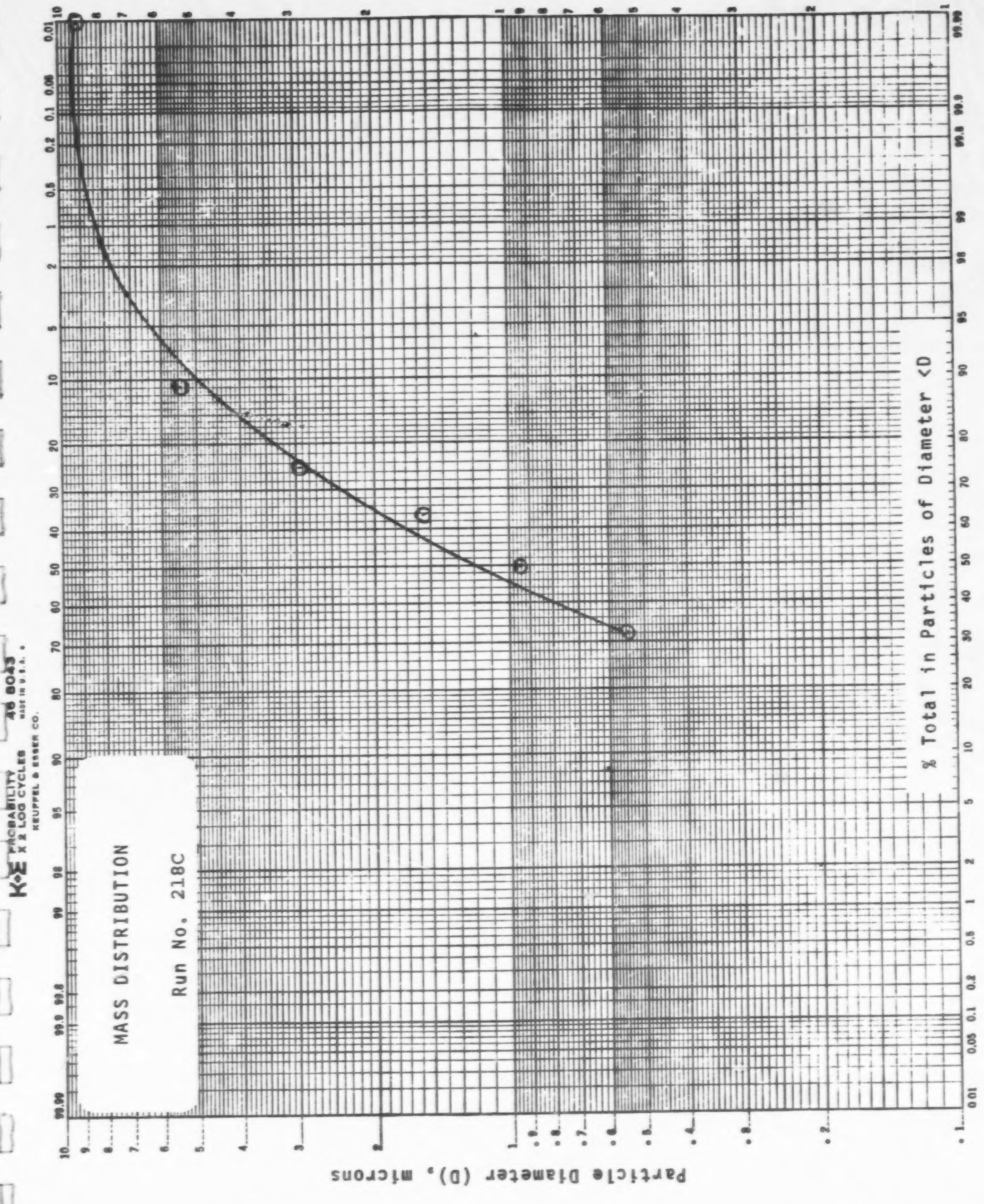
MASS DISTRIBUTION

Run No. 216B


K&E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 216C
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 218A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO. MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 218B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K&E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 218C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO. MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
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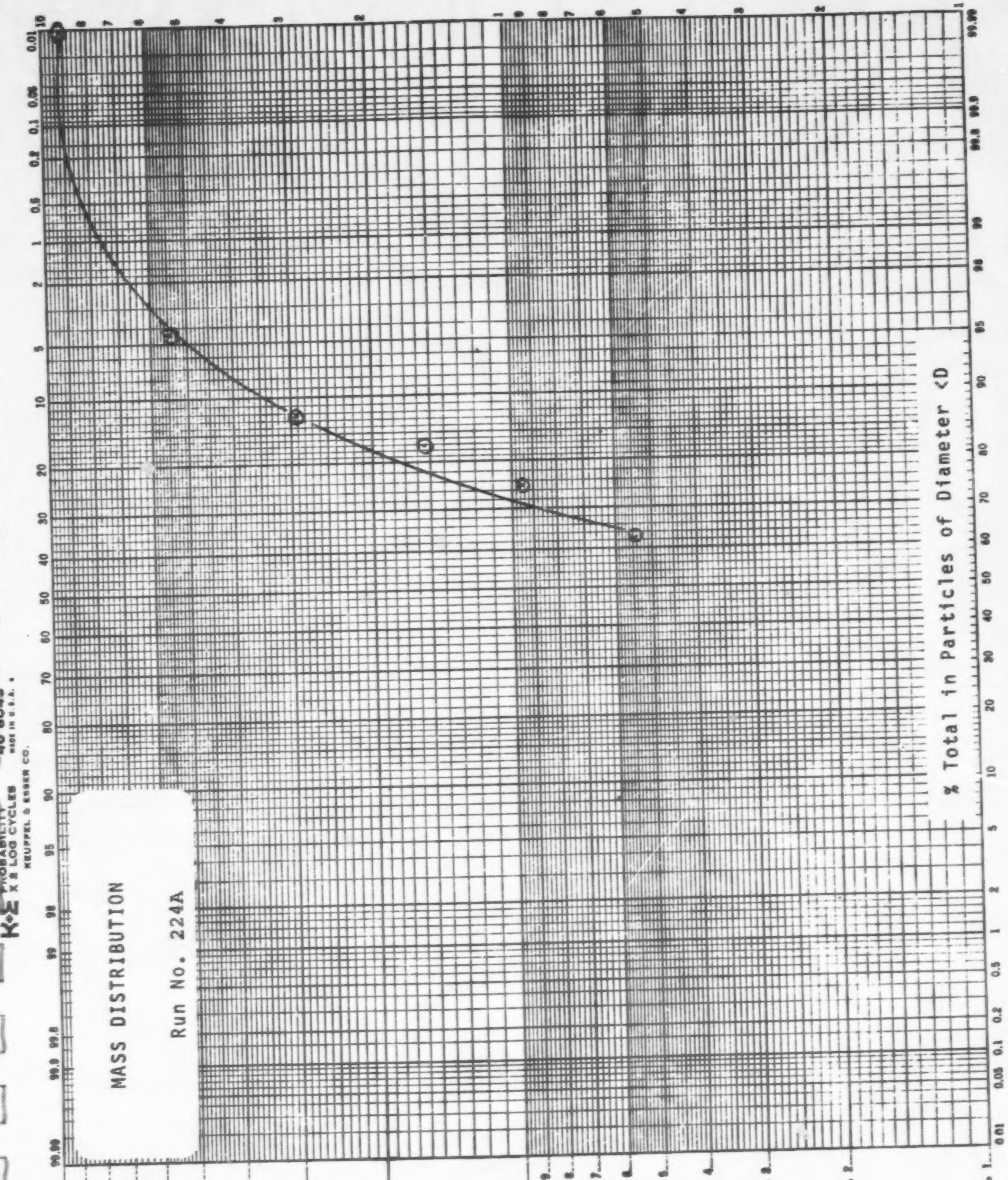
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 224A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
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.5
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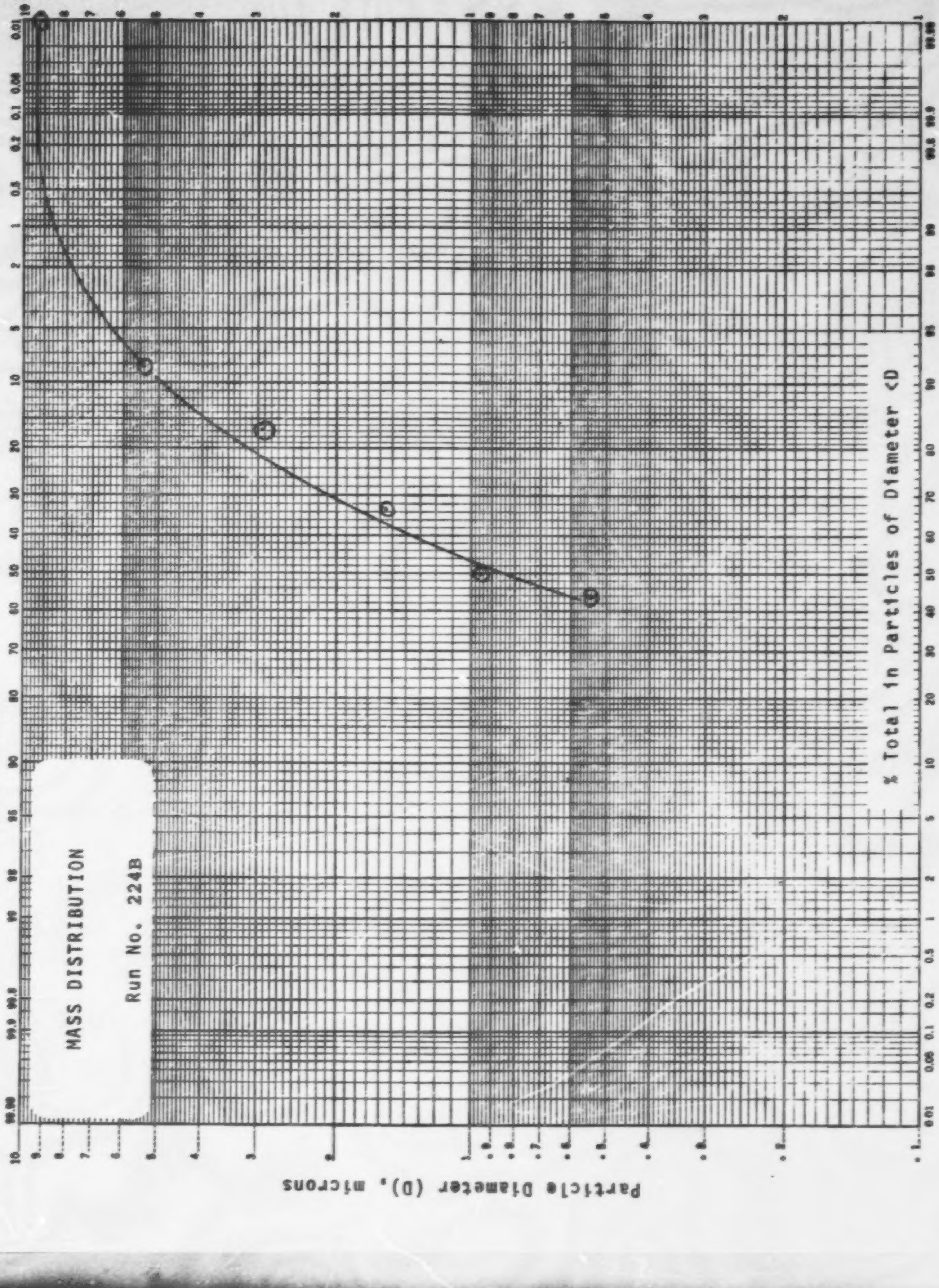
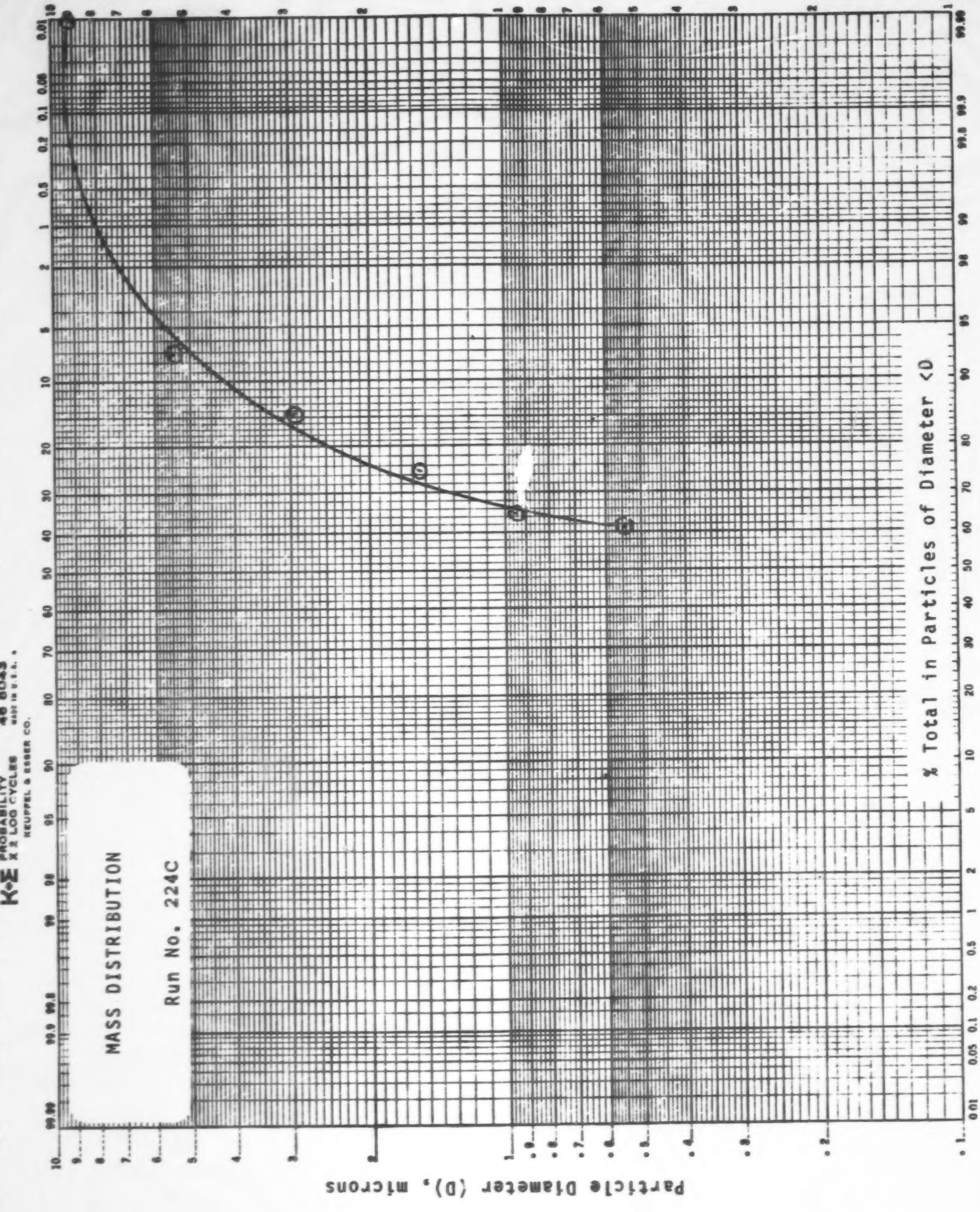
.3
.2
.1


MASS DISTRIBUTION
Run No. 224B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
K-E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO. MADE IN U.S.A.


MASS DISTRIBUTION
Run No. 224C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
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6
5
4
3
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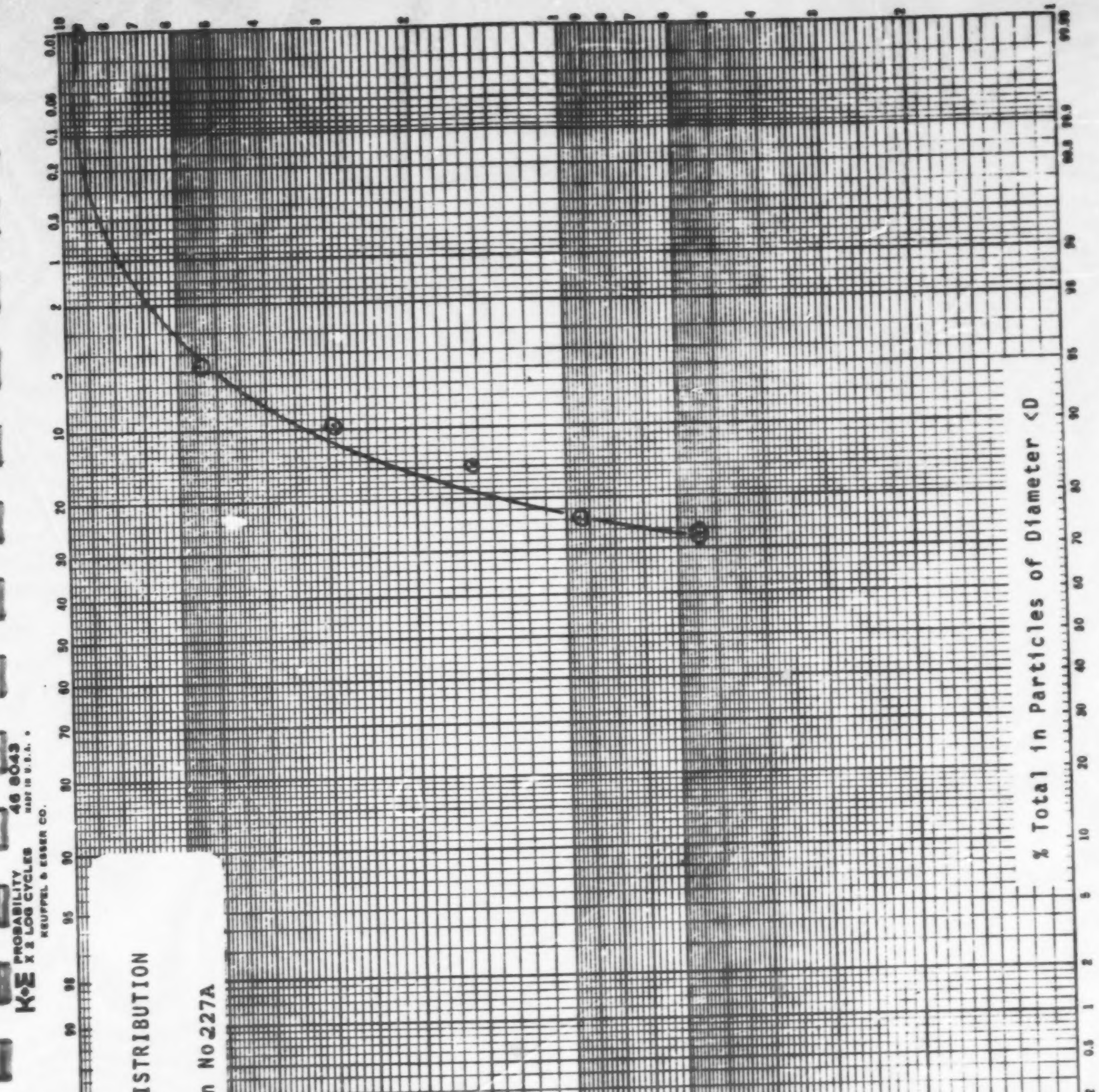
MASS DISTRIBUTION
Run No 227A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
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6
5
4
3
2
1
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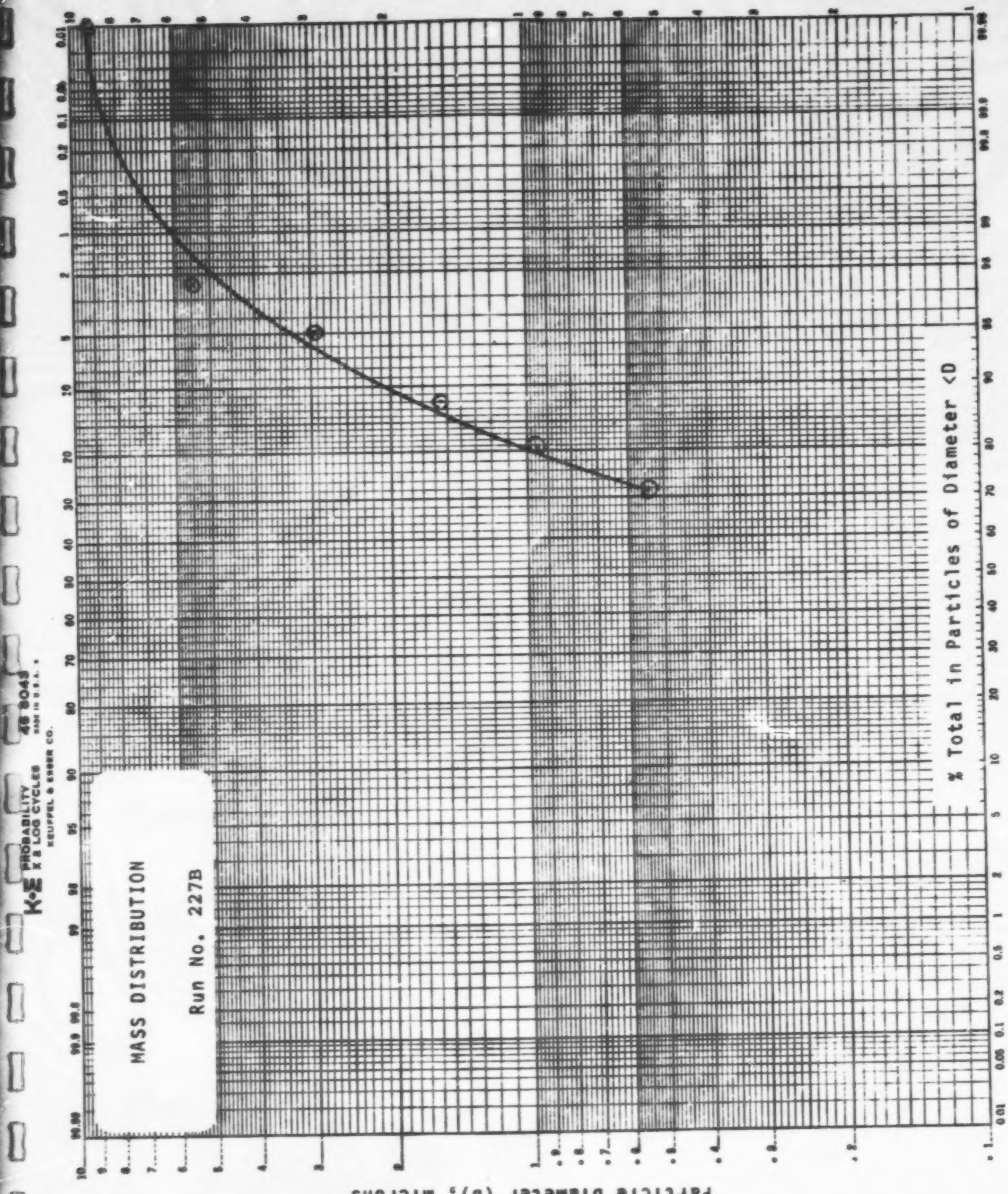
.2
.1
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO. MADE IN U.S.A.


MASS DISTRIBUTION
Run No. 227B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
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7
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4
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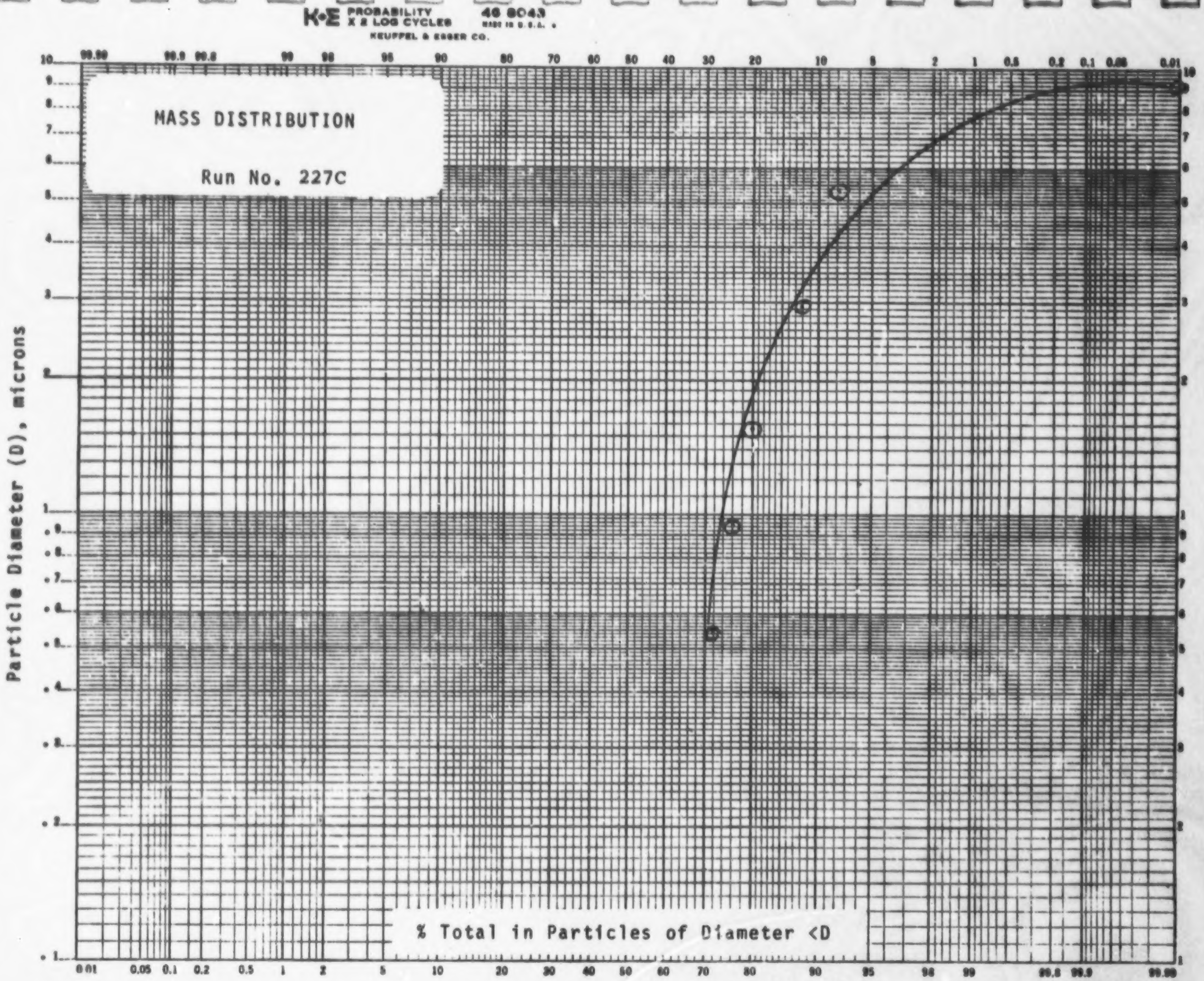
.1


K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 227C
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
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6
5
4
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1
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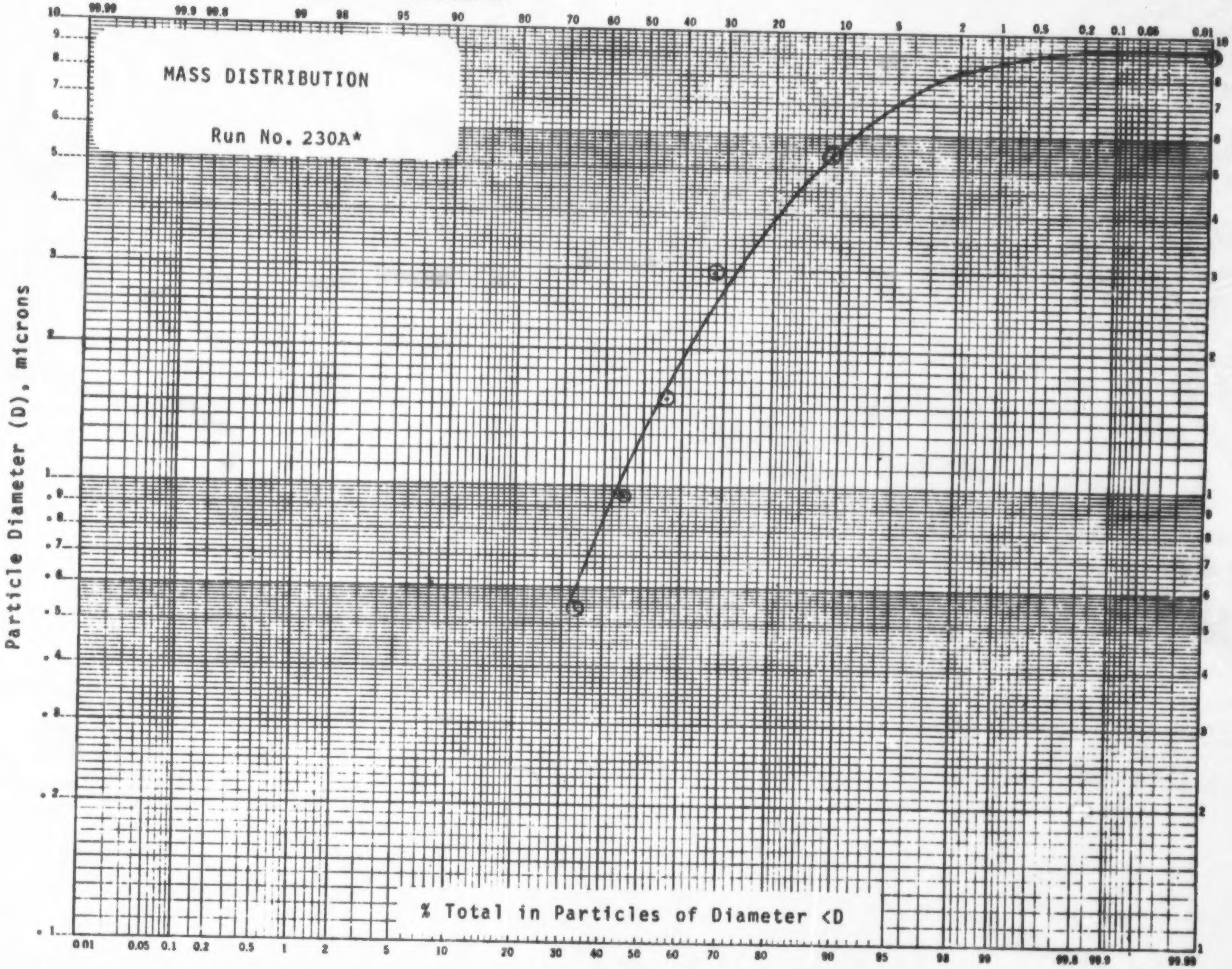
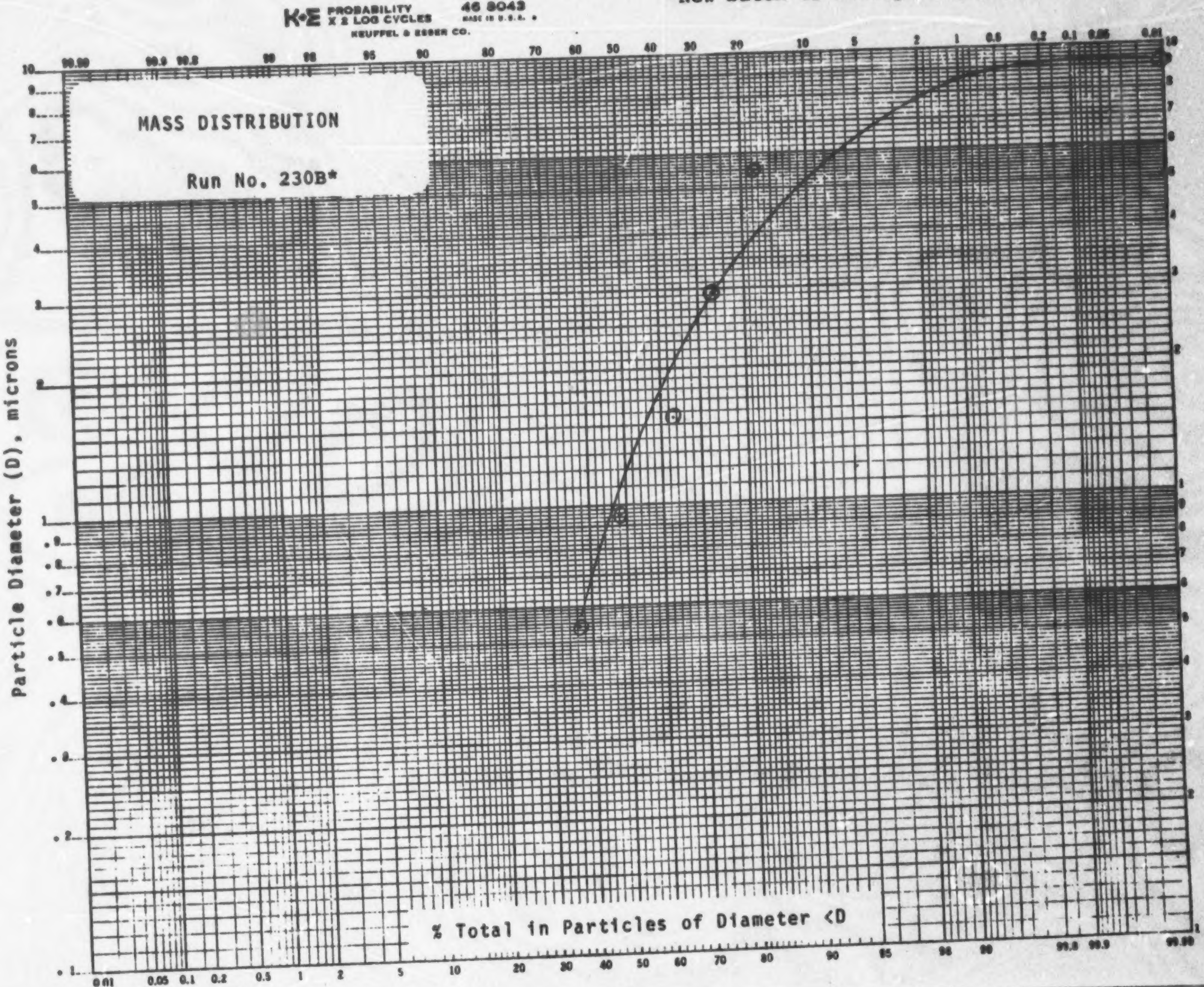
.5
.4
.3
.2
.1

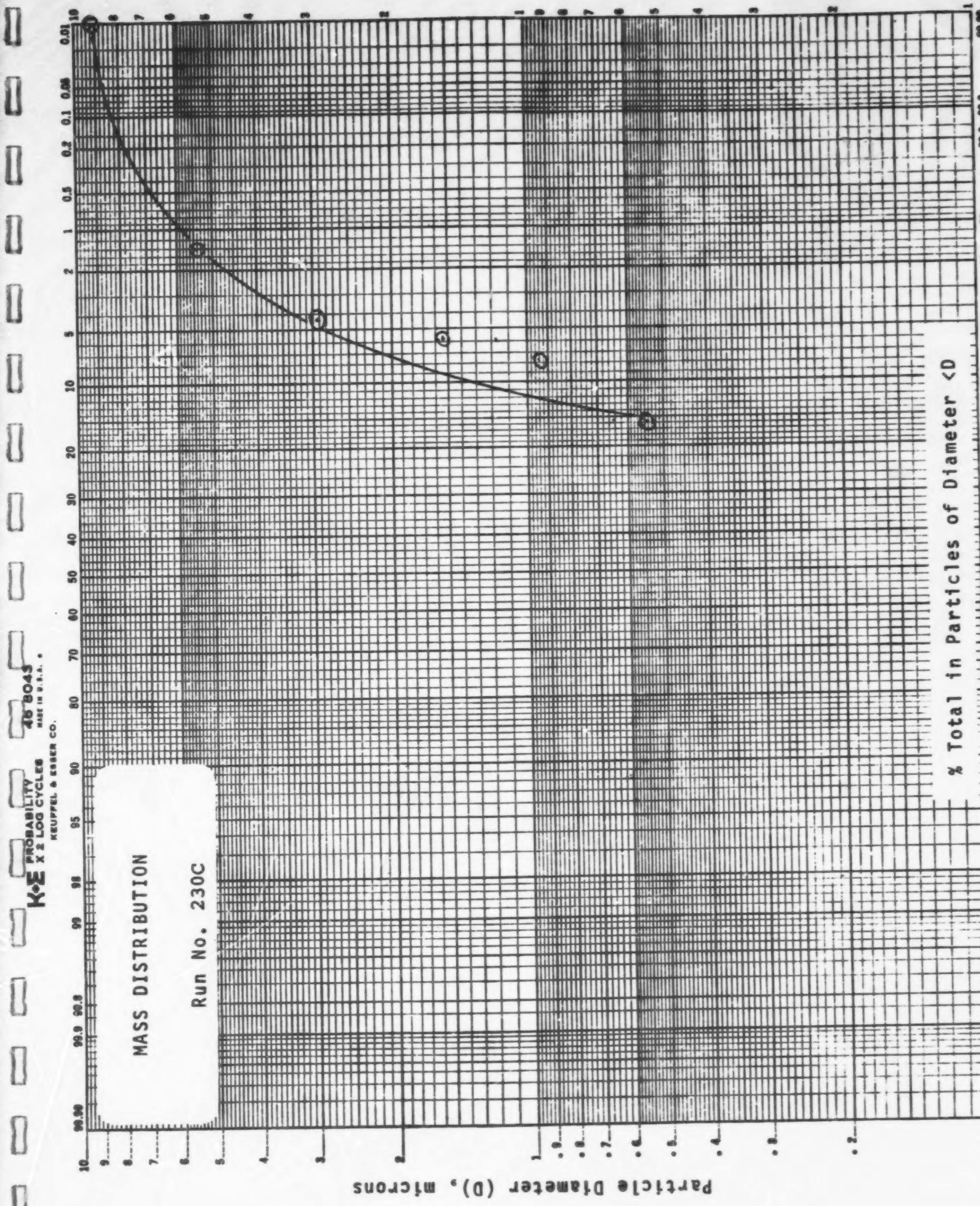
K+E PROBABILITY X 2 LOG CYCLES 46 8043 MADE IN U.S.A. KEUFFEL & ESSER CO.

*New batch of millipore wts are very low.



*New batch of millipore paper wts low.




MASS DISTRIBUTION
Run No. 230C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
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4
3
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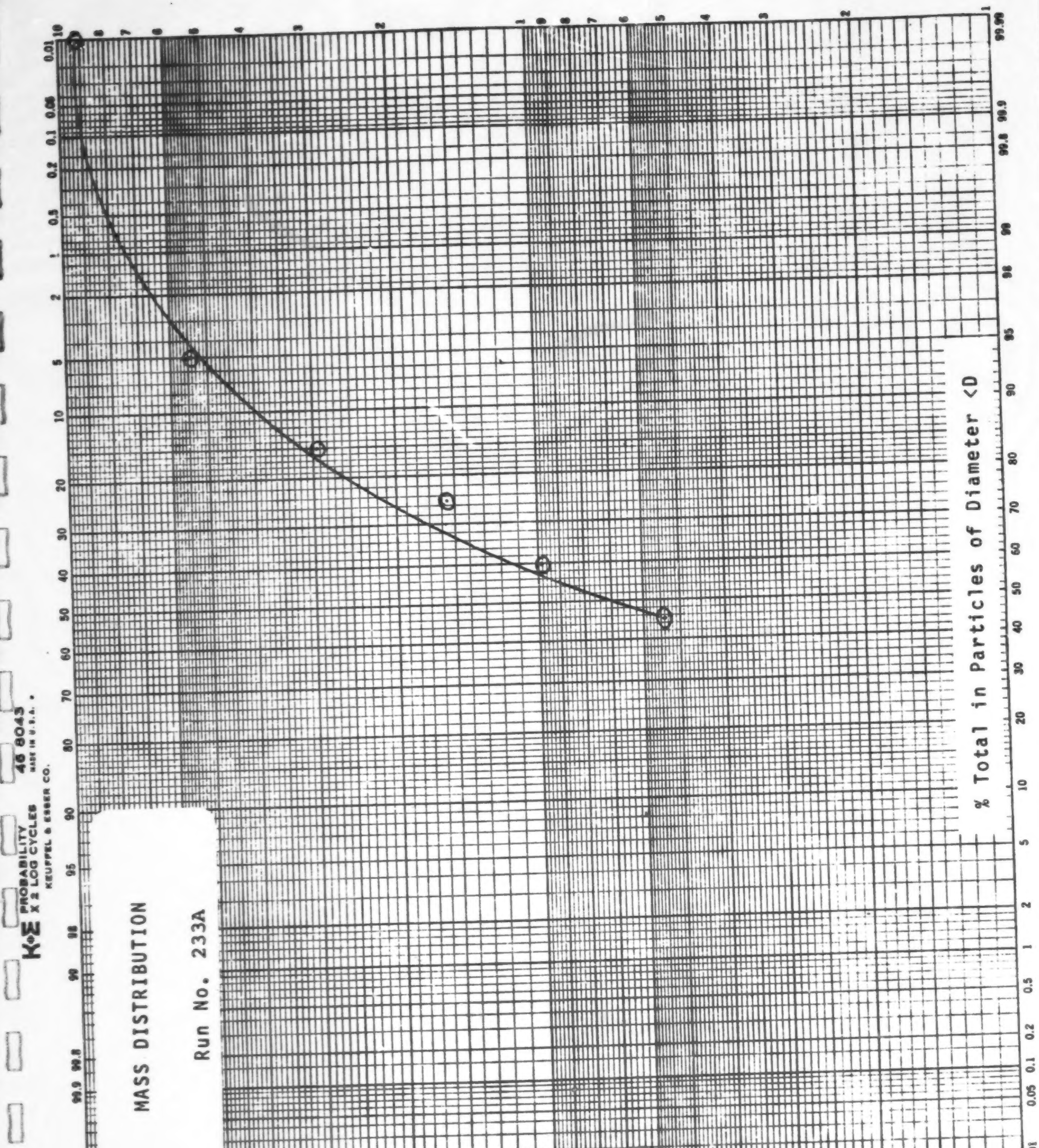
.6
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 233A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
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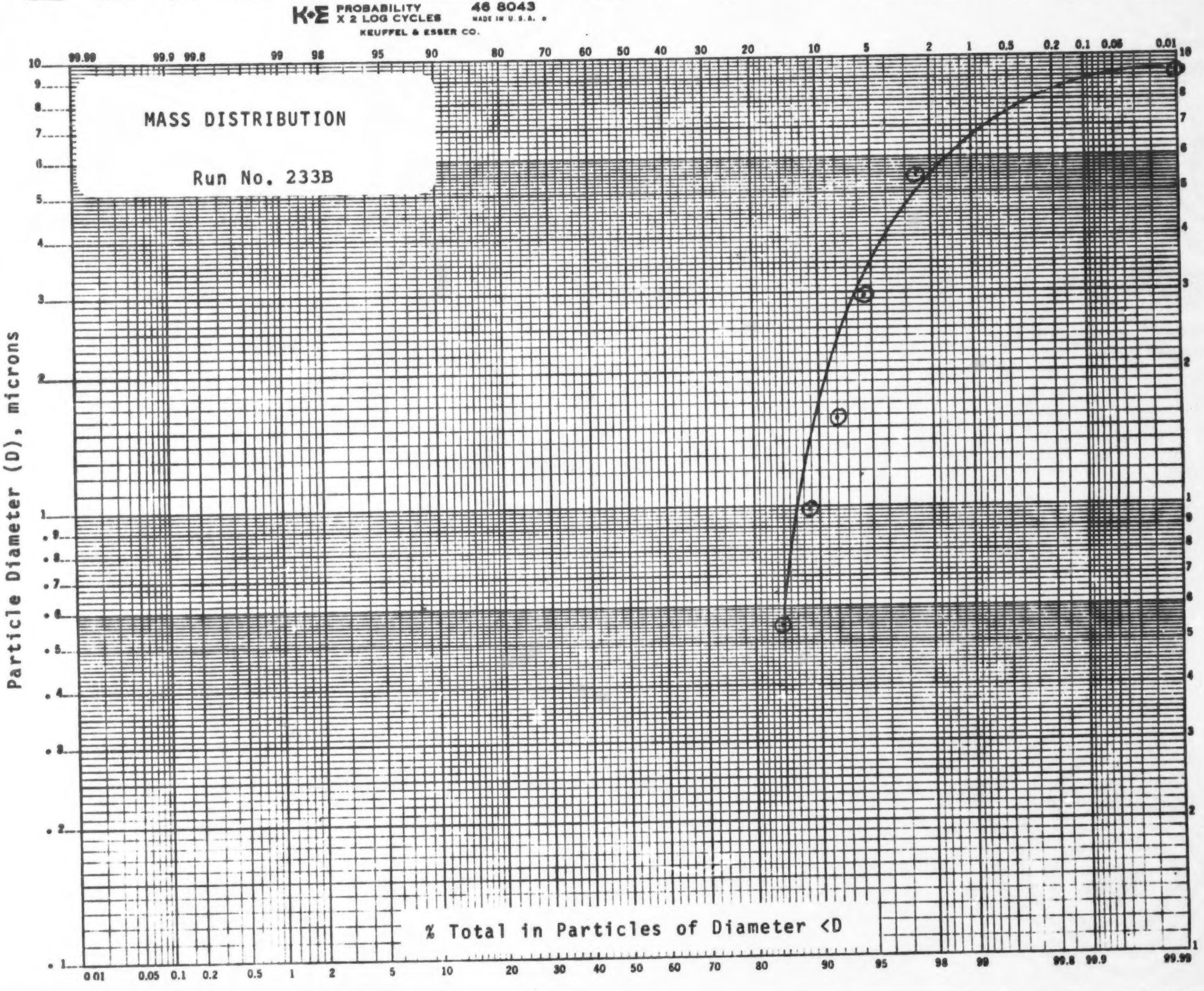
.1


K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 233B
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
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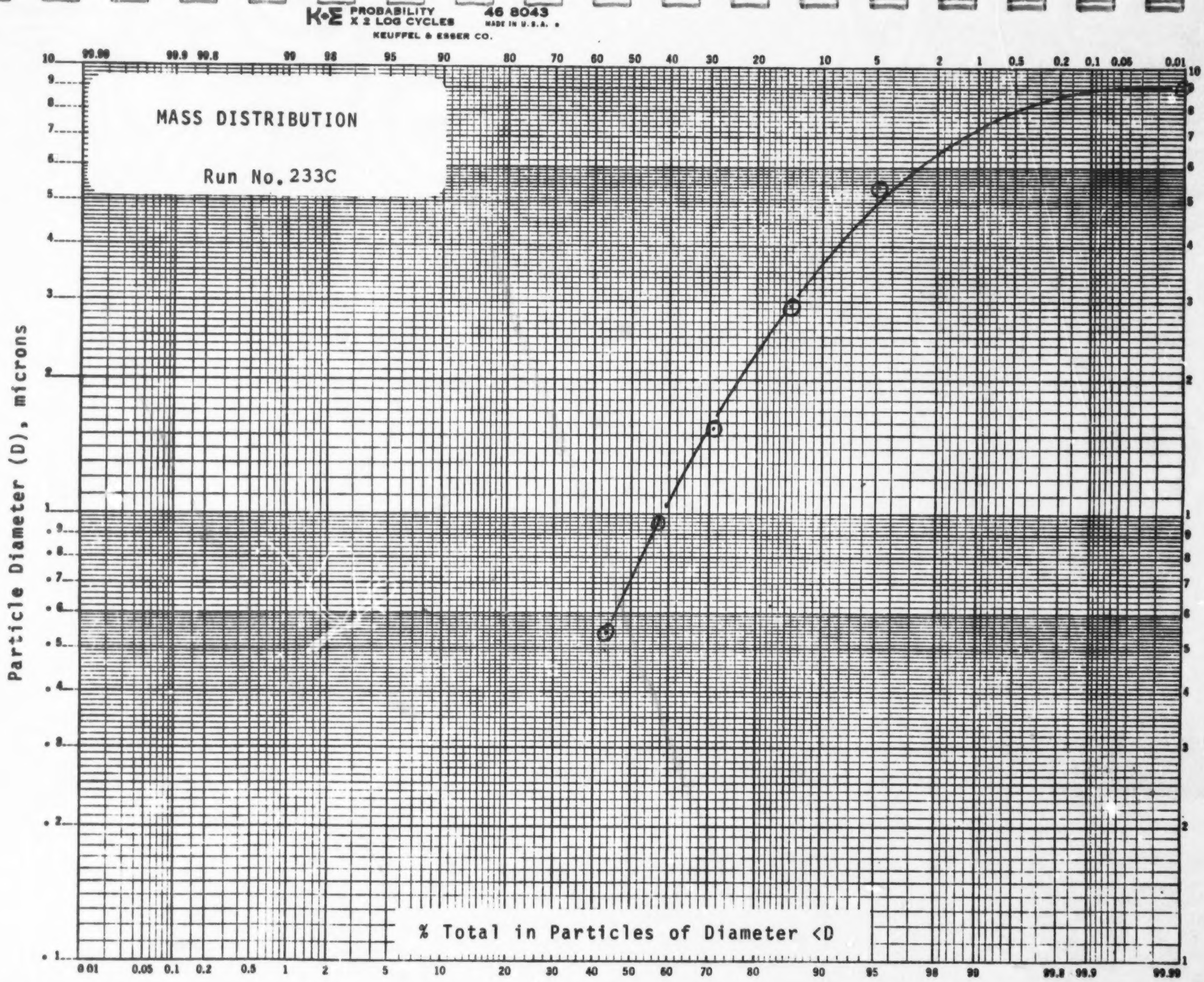
.1


K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 233C
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
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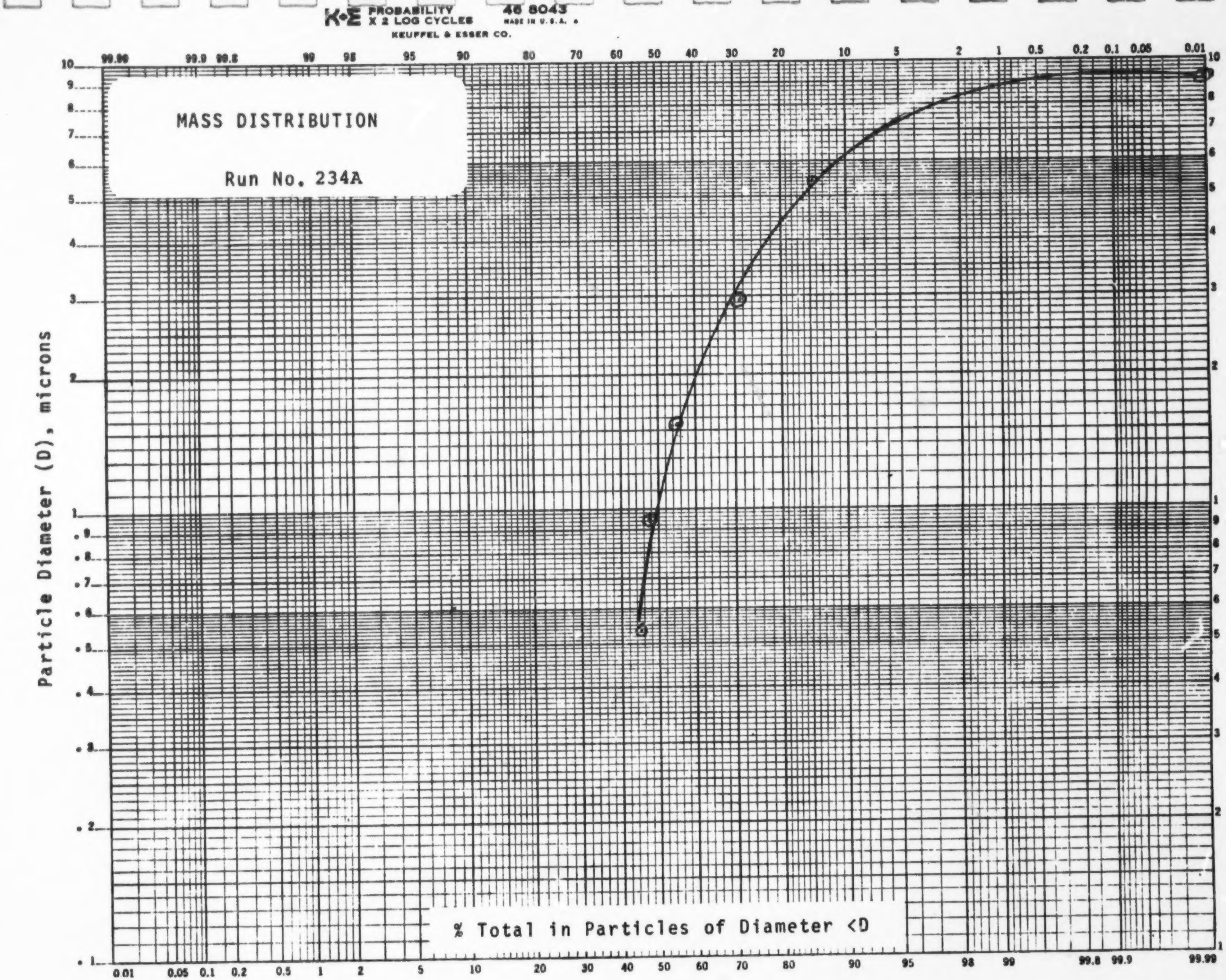
K+E PROBABILITY X 2 LOG CYCLES 46 8043 MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 234A
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
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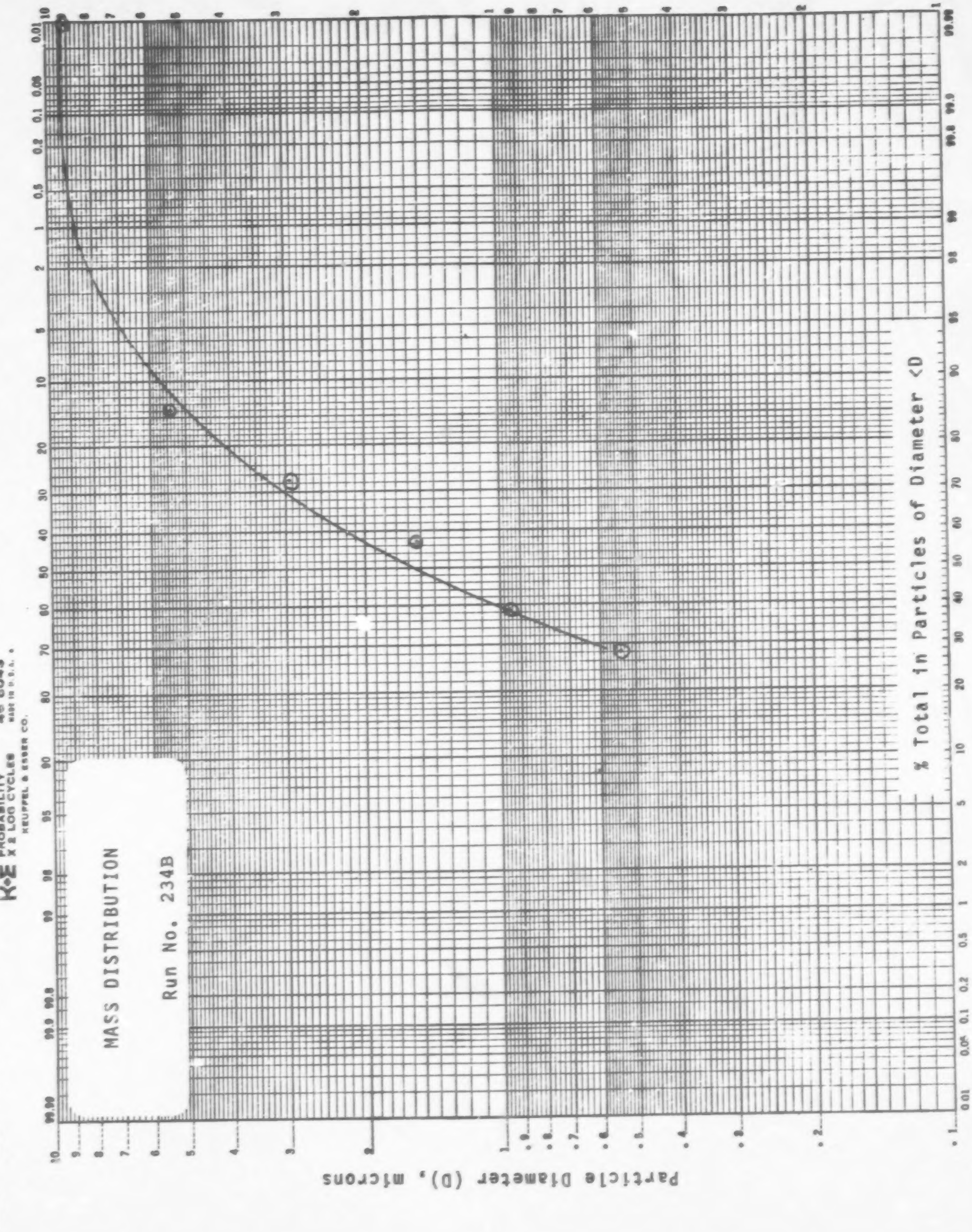
.1


MASS DISTRIBUTION
Run No. 234B
Particle Diameter (D), microns
% Total in Particles of Diameter <D
K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
10
9
8
7
6
5
4
3
2
1
.9
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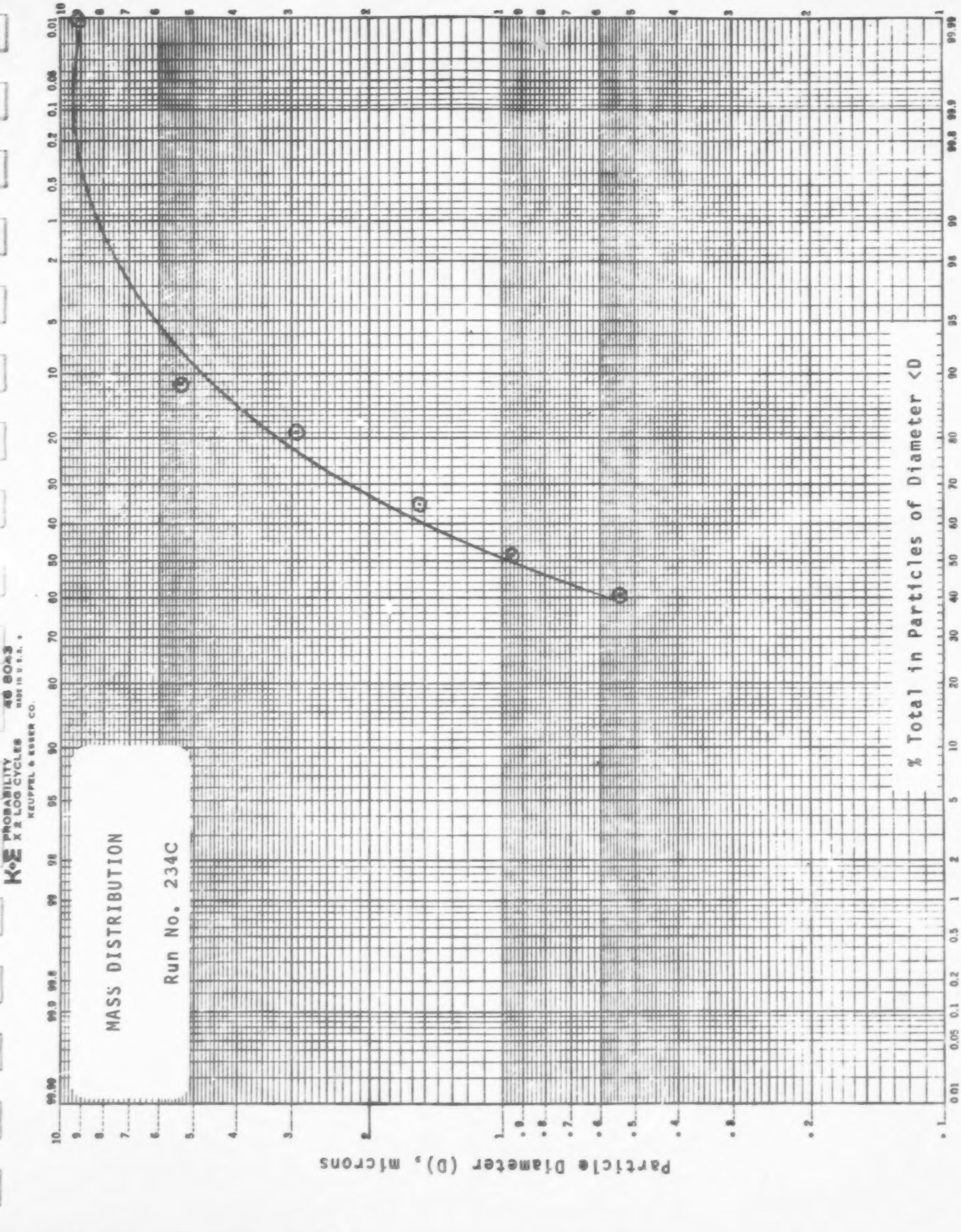
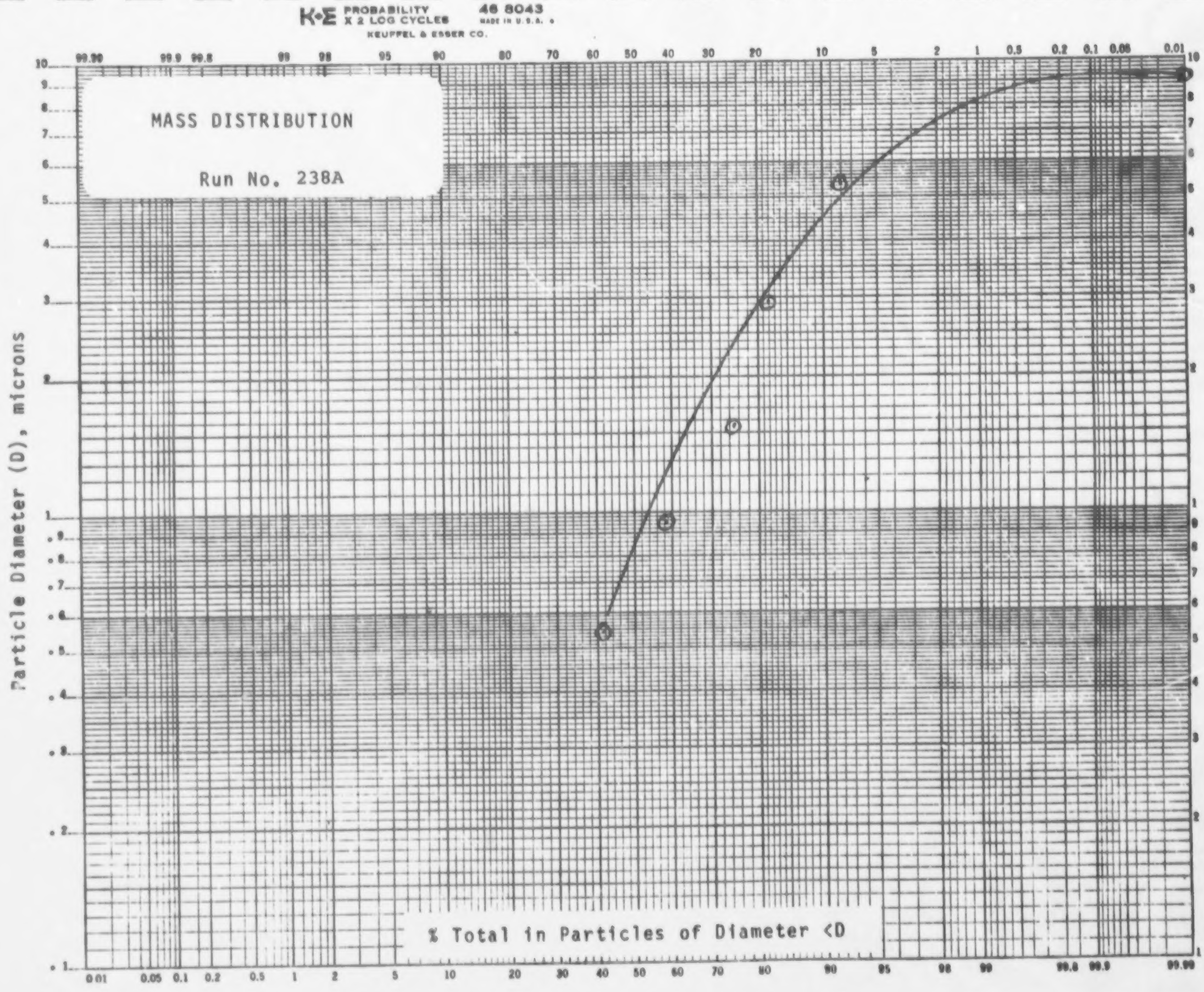
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99


MASS DISTRIBUTION
Run No. 234C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
MADE IN U.S.A.


K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 238A
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
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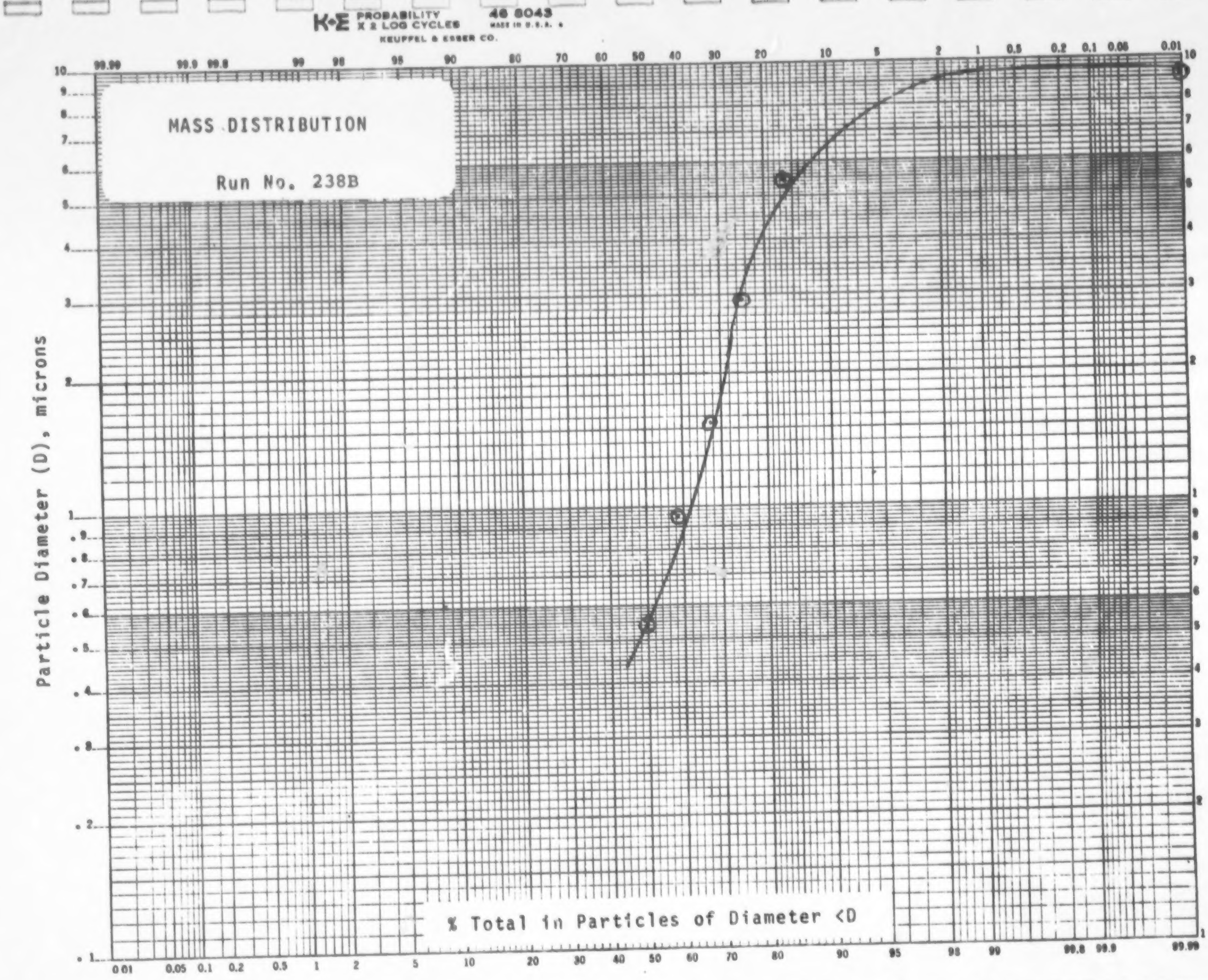
.6
.5
.4
.3
.2
.1


K+E PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
46 8043
MADE IN U.S.A.
MASS DISTRIBUTION
Run No. 238B
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
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5
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.5
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.3
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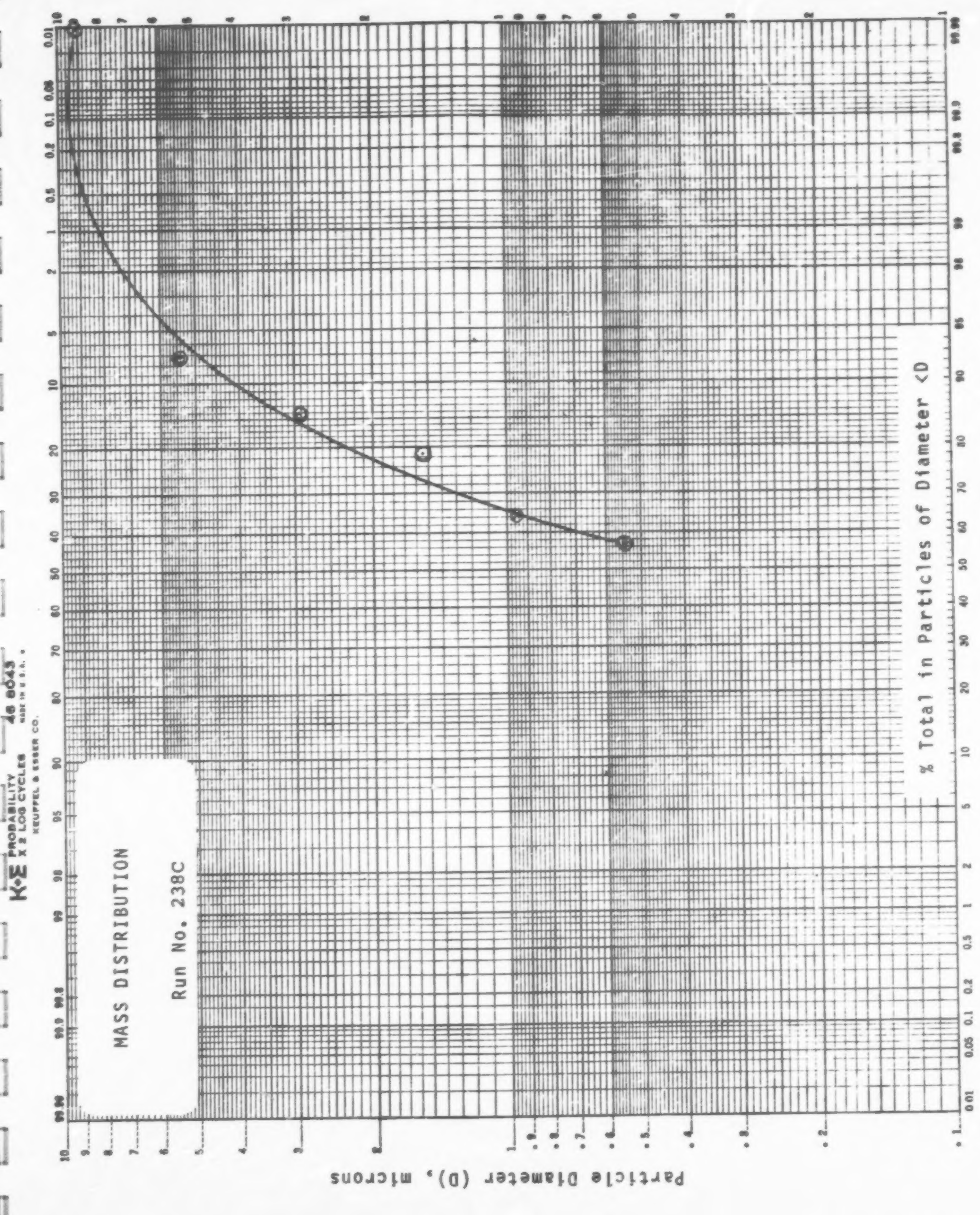
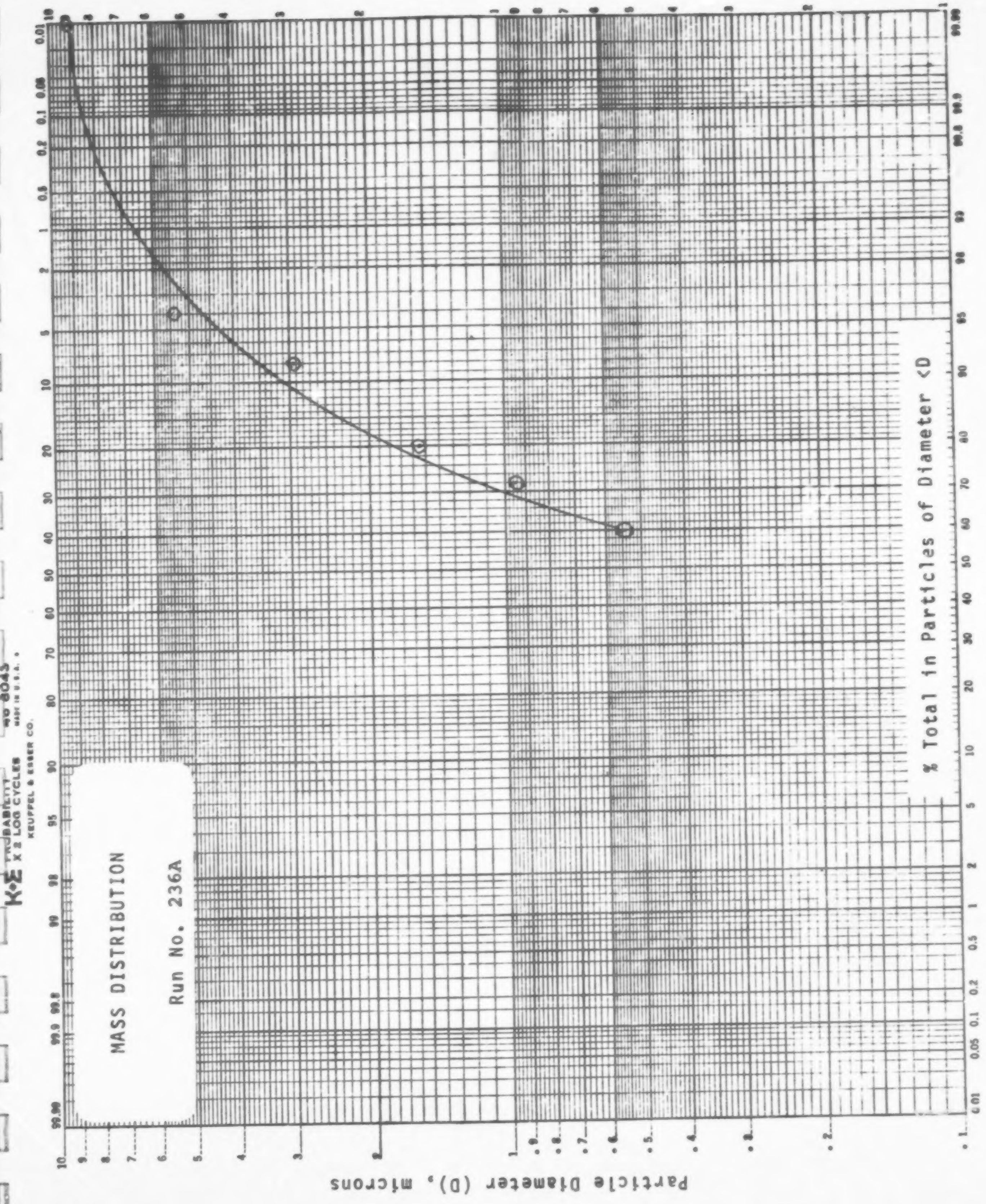
.1


MASS DISTRIBUTION
Run No. 238C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.


MASS DISTRIBUTION
Run No. 236A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
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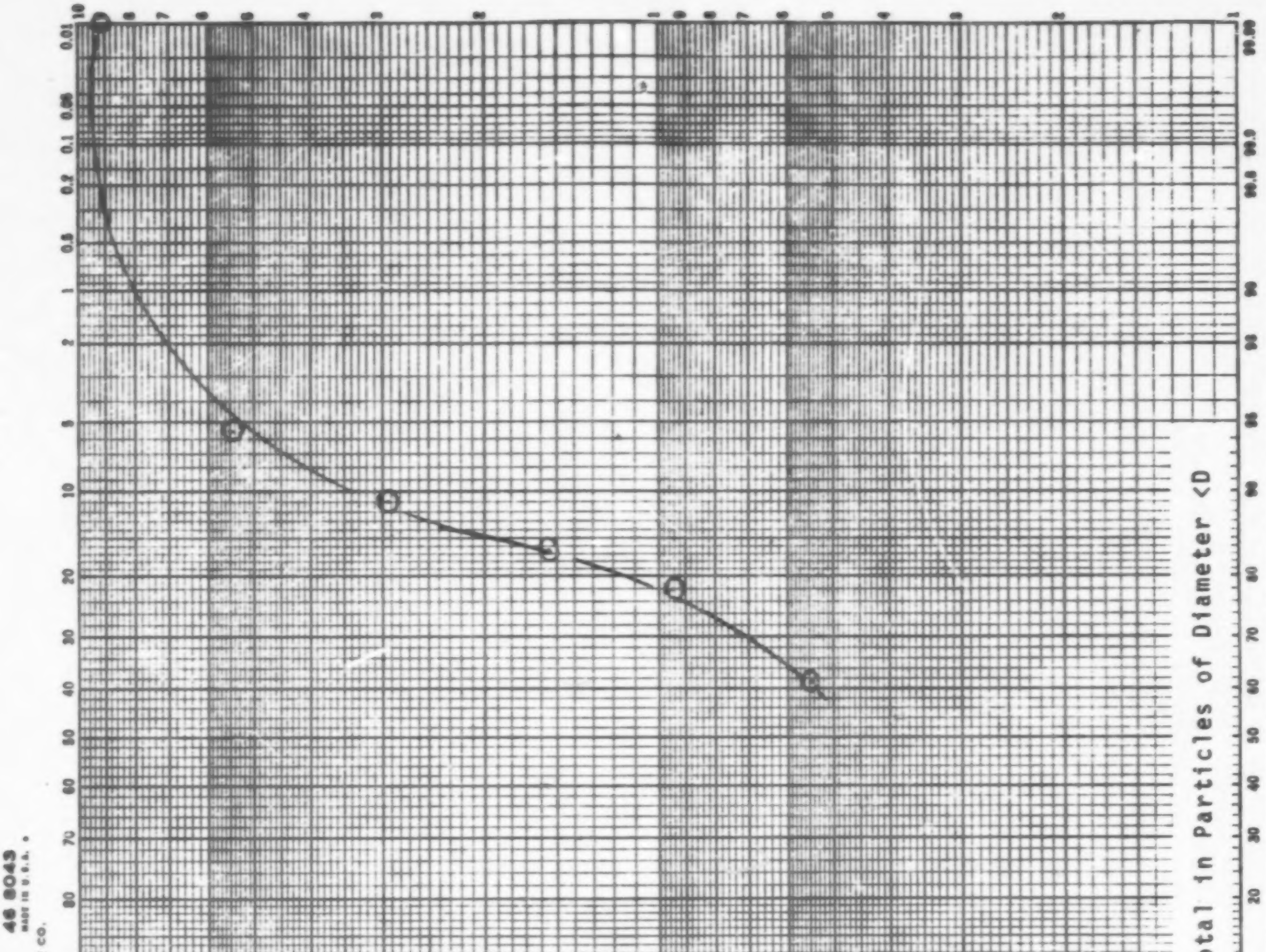
K·E PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
46 8043
MADE IN U.S.A.


MASS DISTRIBUTION
Run No. 236B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
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.4
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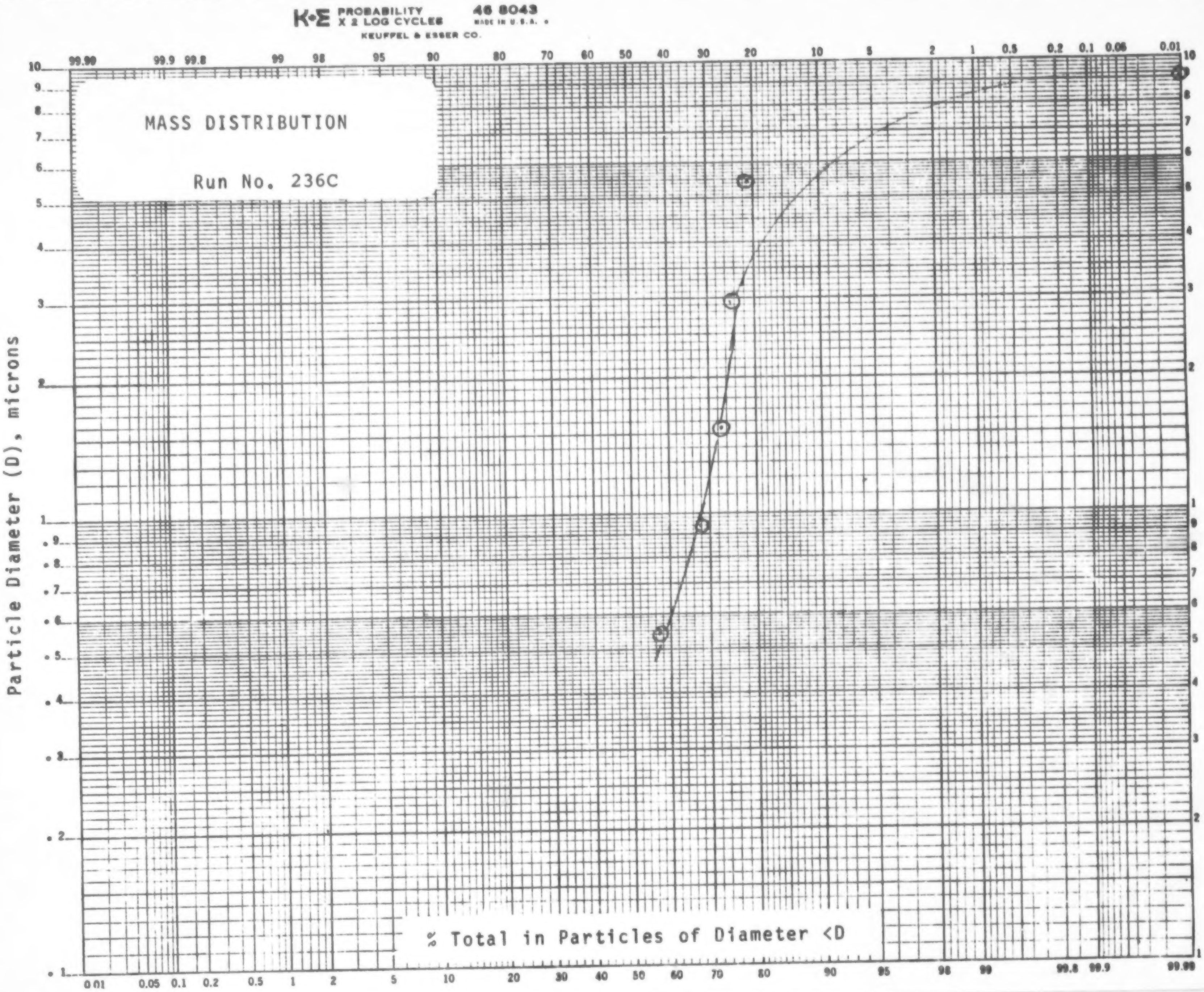
K·E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO. MADE IN U.S.A.
MASS DISTRIBUTION
Run No. 236C
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
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4
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.5
.4
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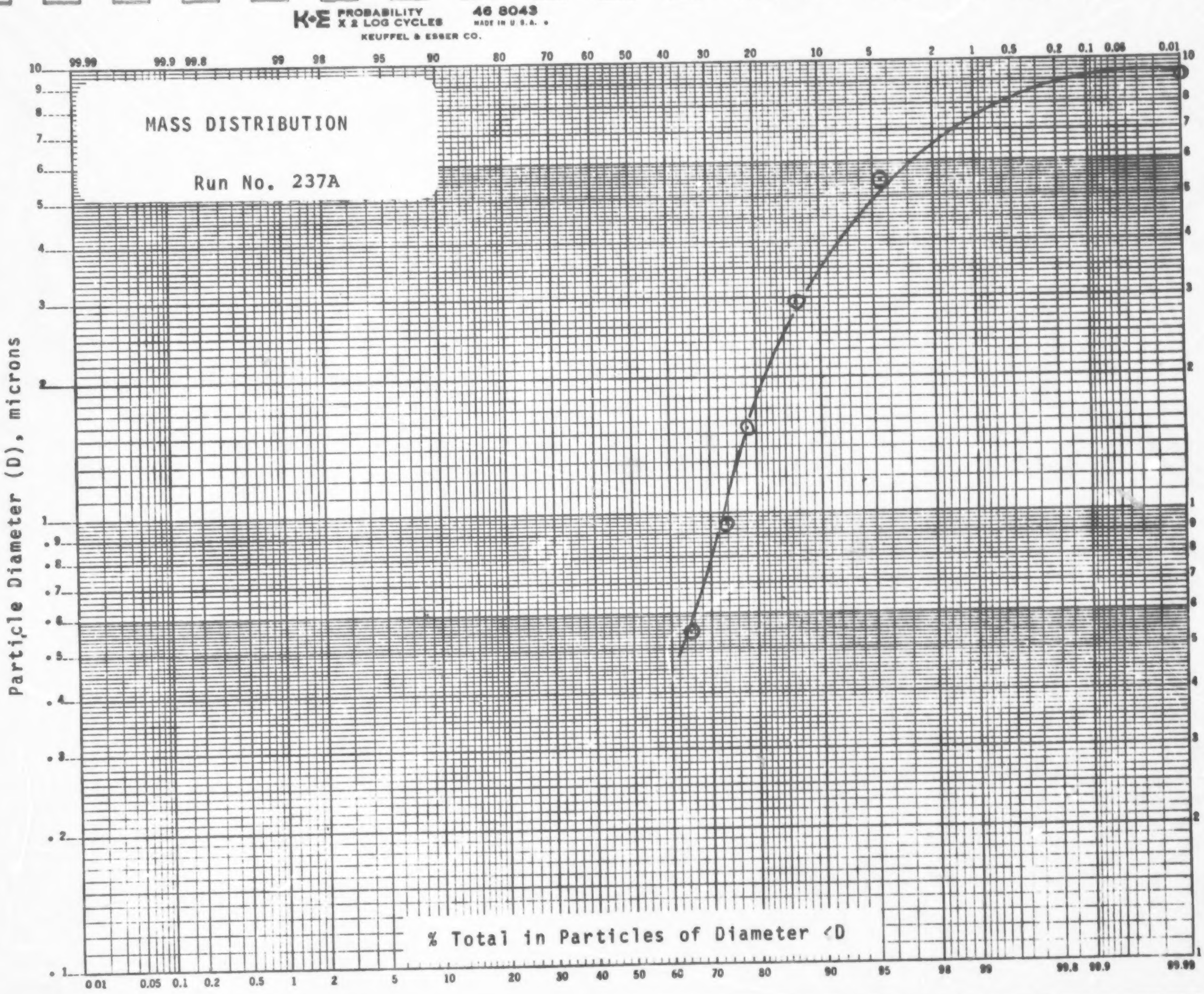
K+E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 237A
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
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10
5
2
1
0.5
0.2
0.1
0.05
0.01
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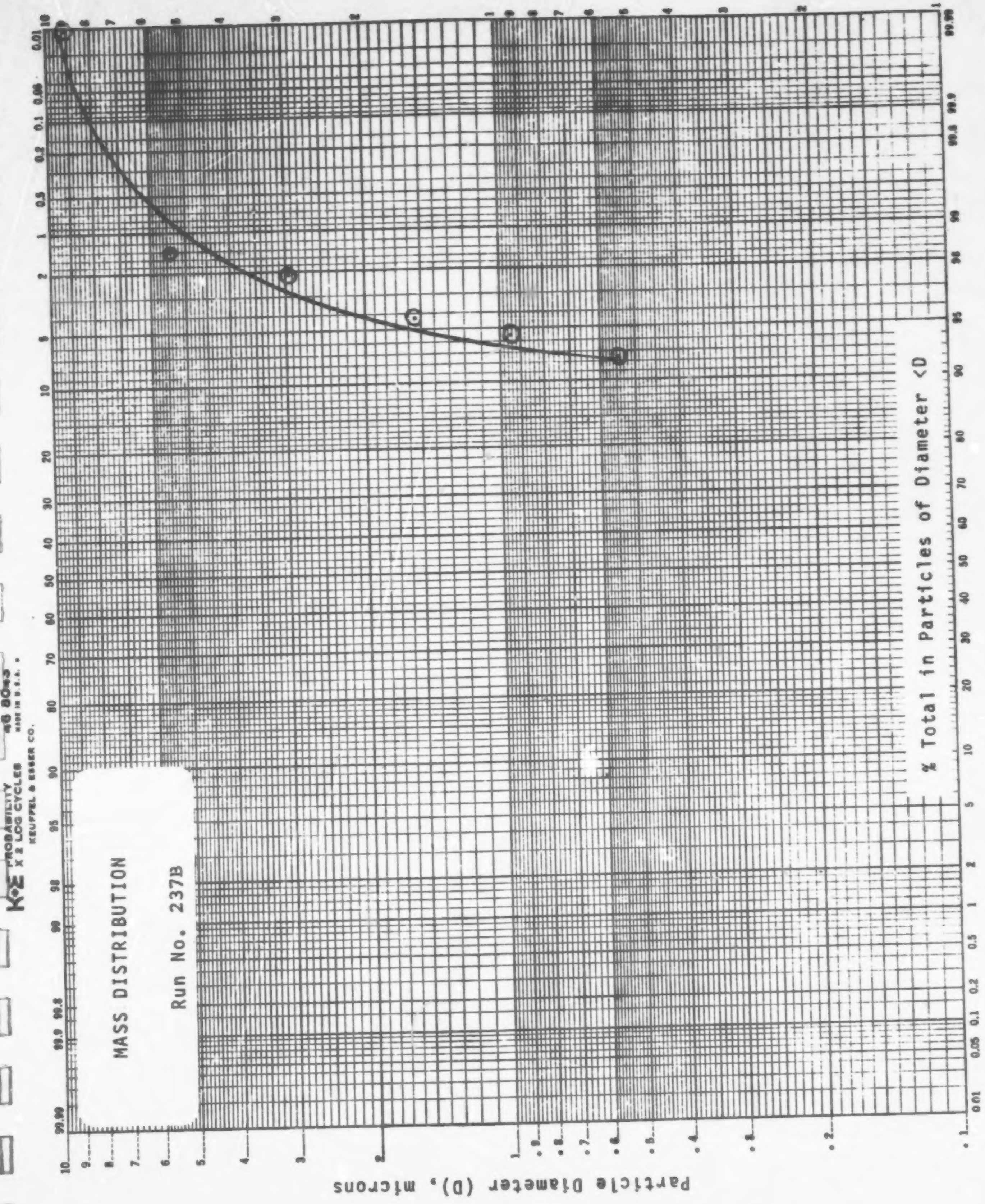
MASS DISTRIBUTION
Run No. 237B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO. MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
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60
70
80
90
95
98
99
99.8
99.9
99.99
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.2
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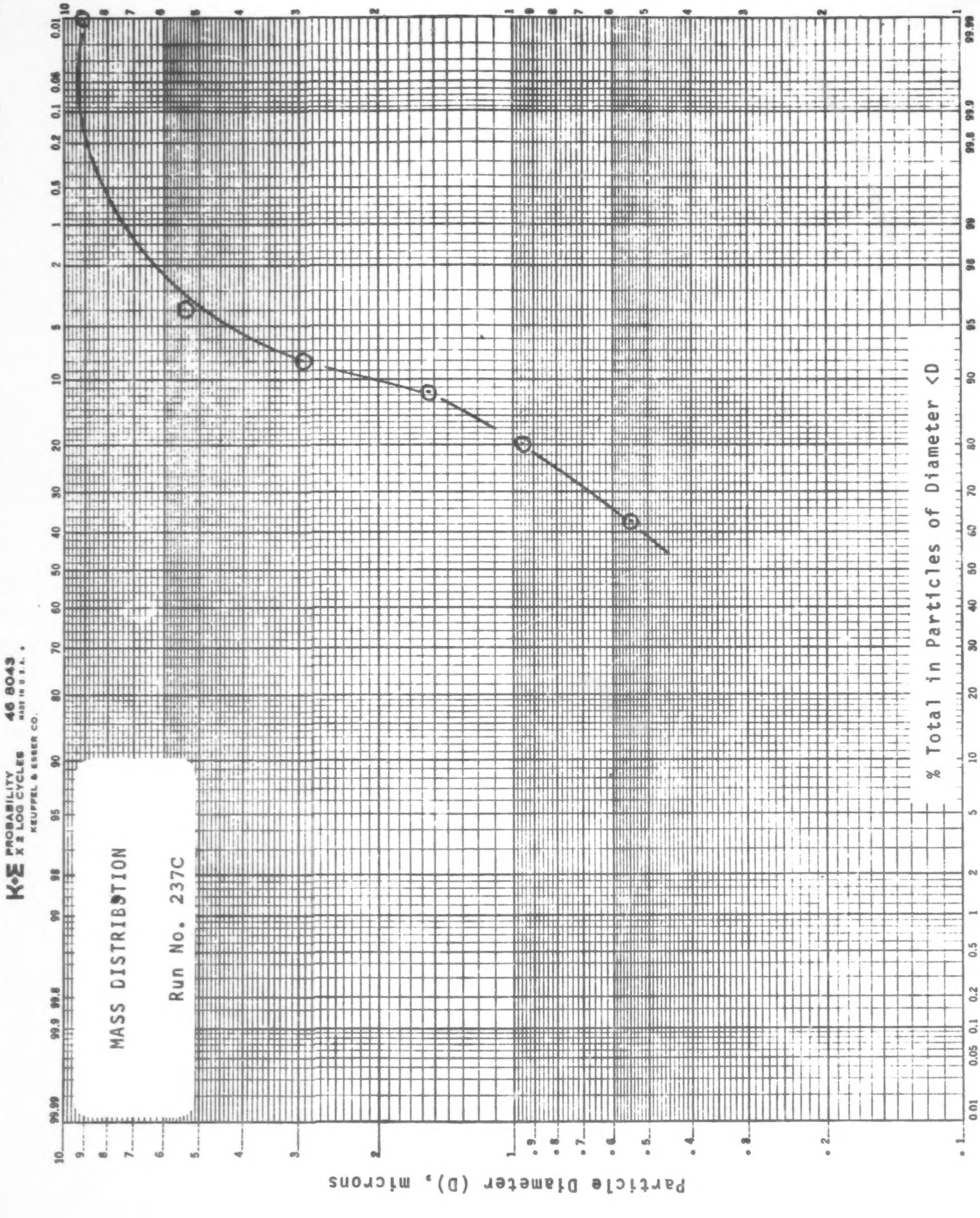
MASS DISTRIBUTION
Run No. 237C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
0.01
0.05
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0.2
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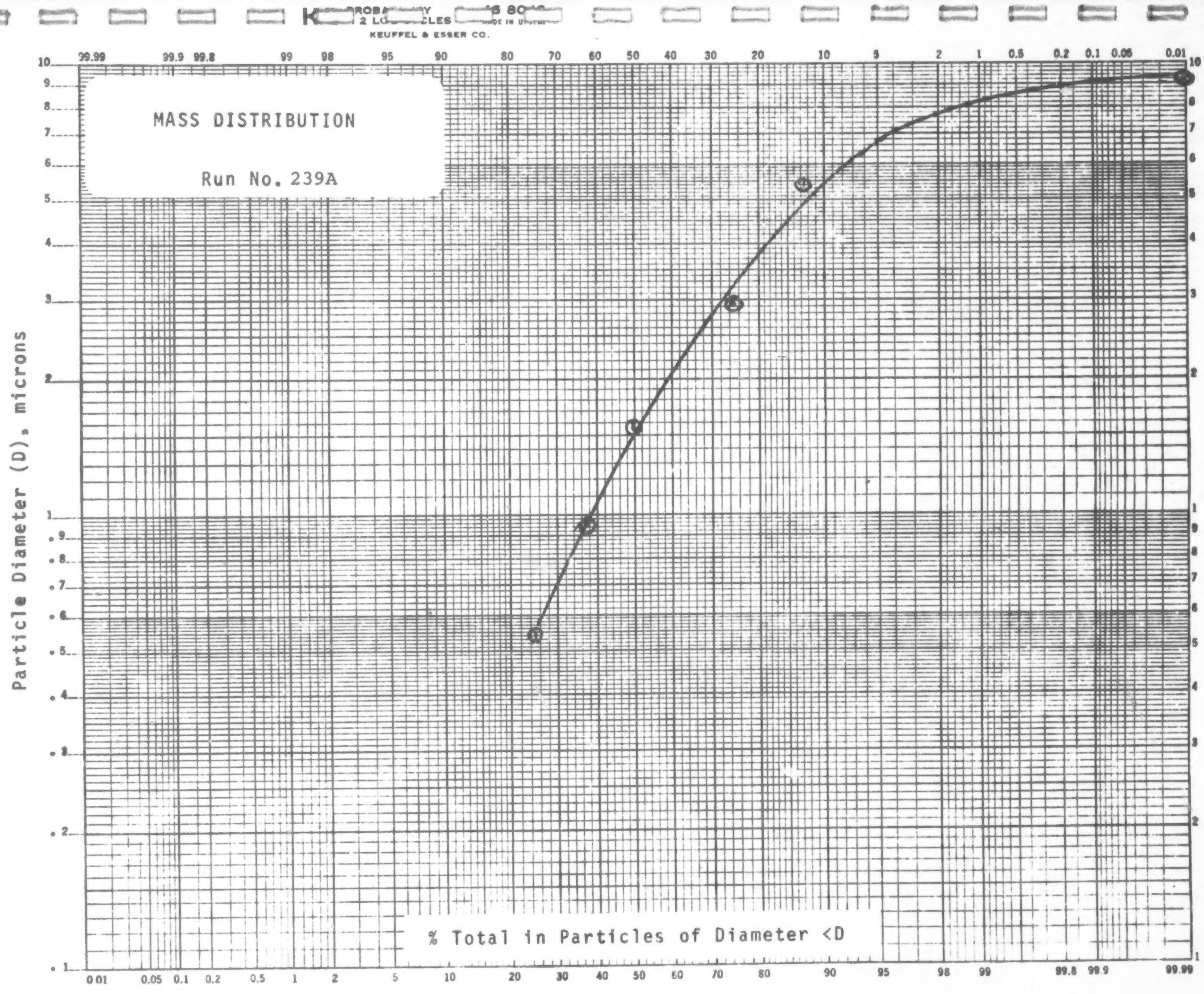
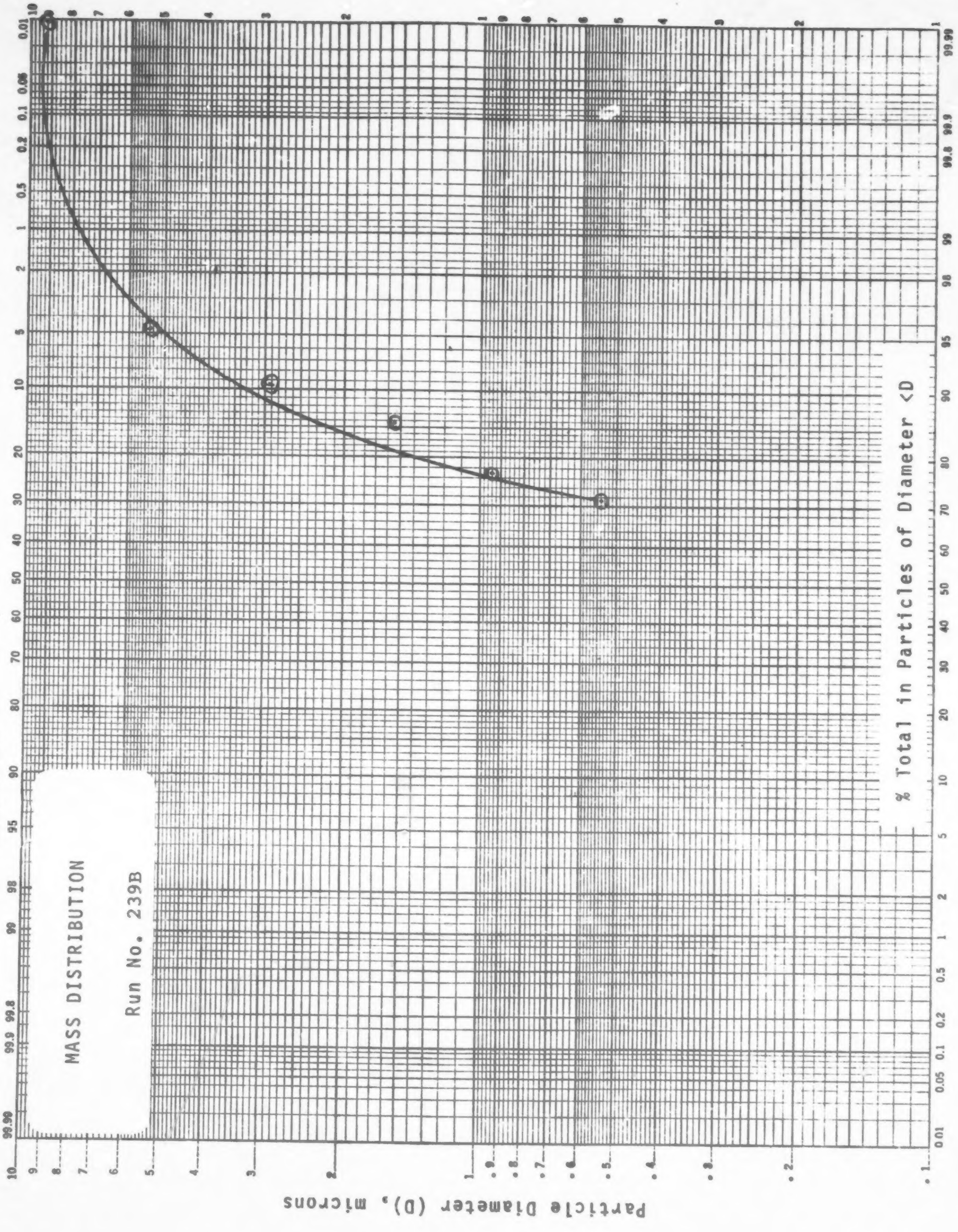
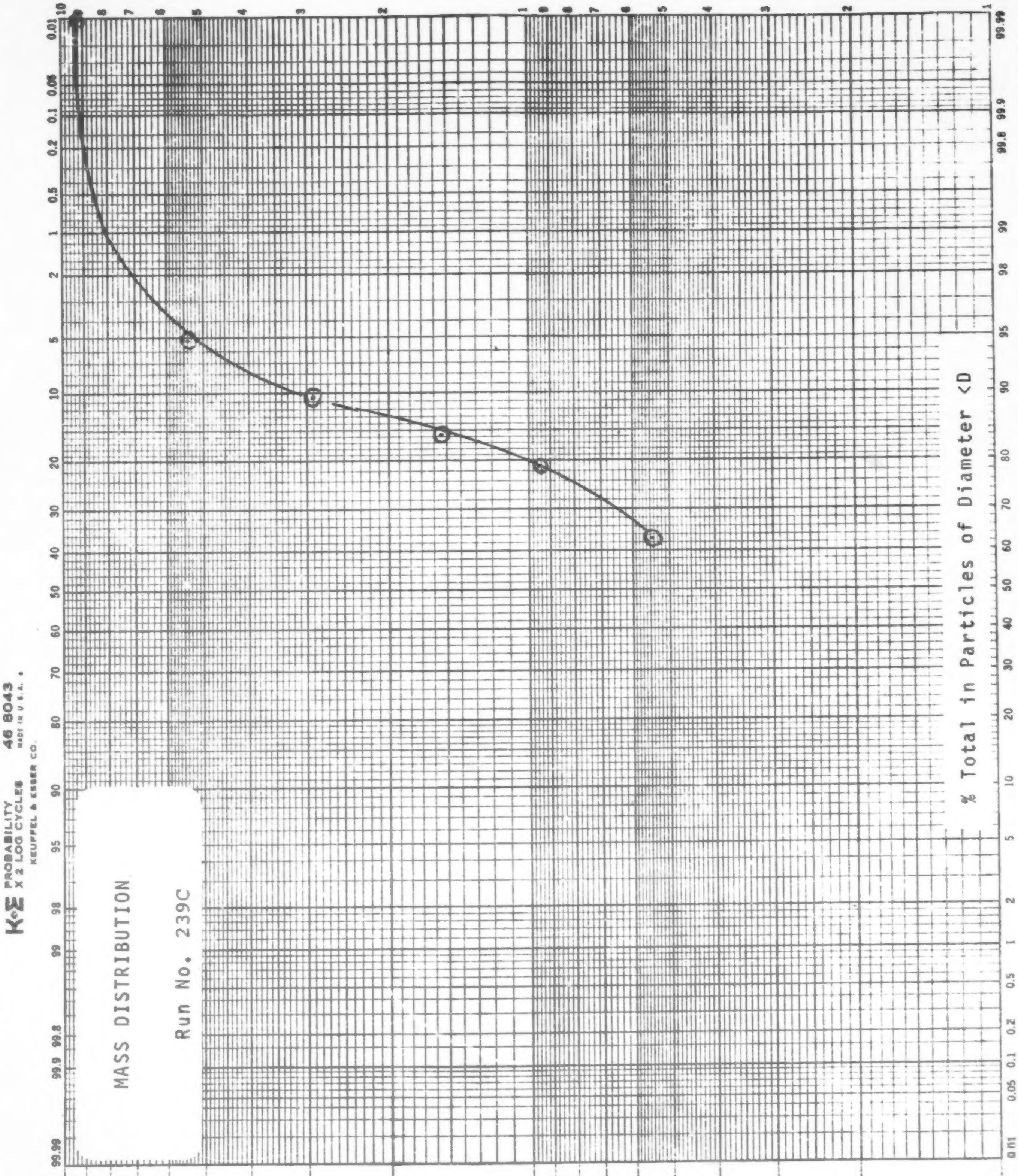

MASS DISTRIBUTION

Run No. 239A



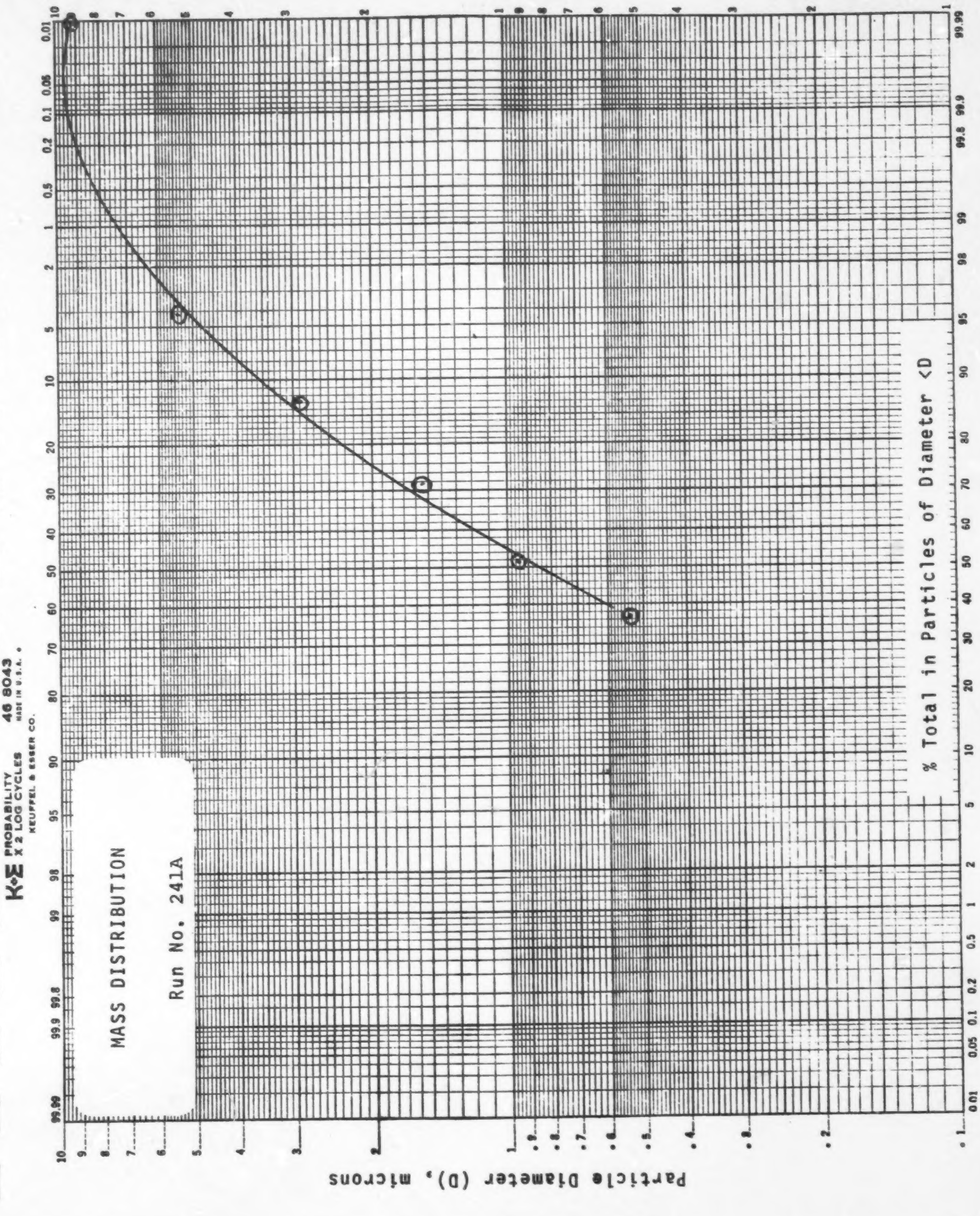
MASS DISTRIBUTION

Run No. 239B



MASS DISTRIBUTION

Run No. 239C


MASS DISTRIBUTION
Run No. 241A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
0.01
0.05
0.1
0.2
0.5
1
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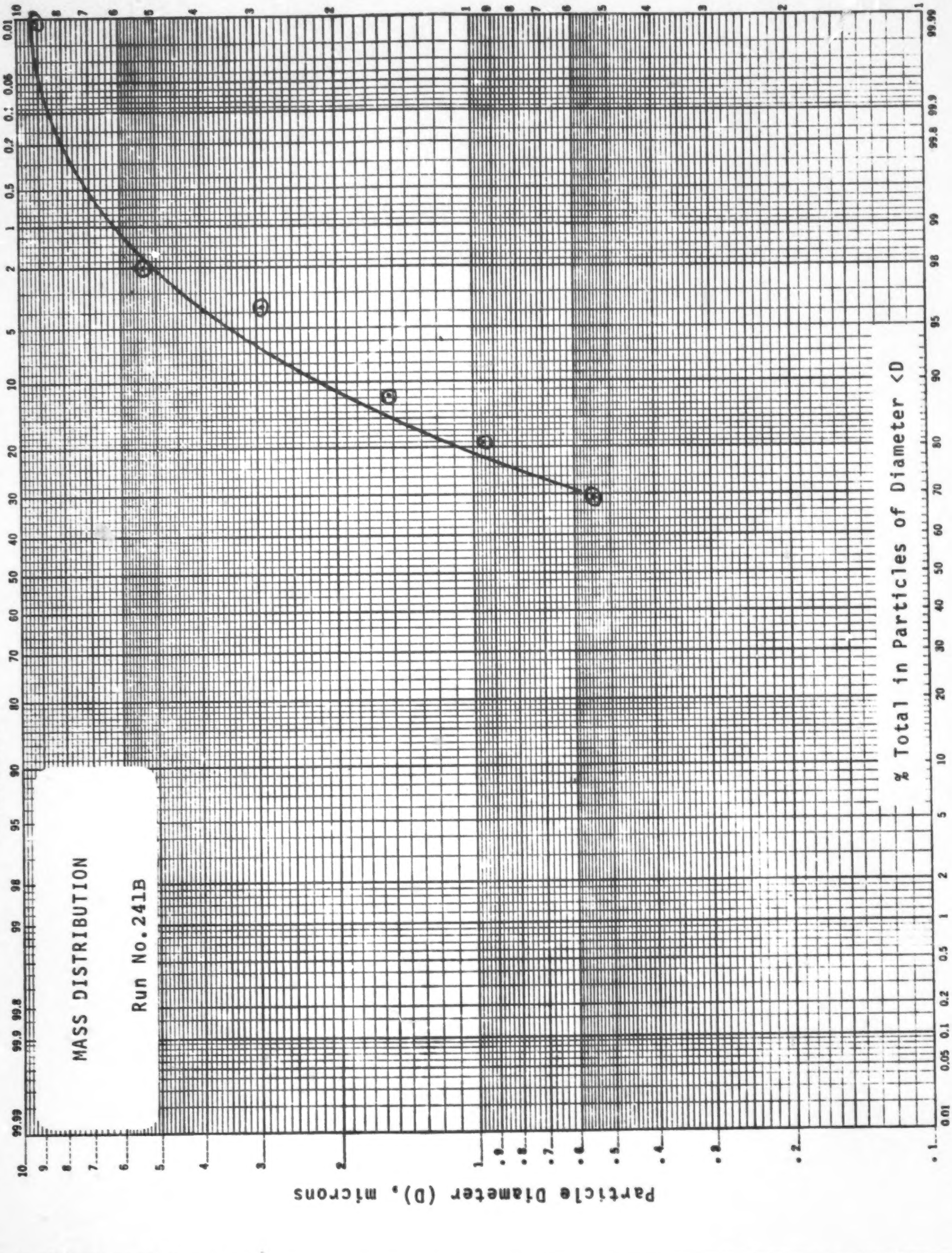
K+E PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
46 8043
MADE IN U.S.A.


MASS DISTRIBUTION
Run No.241B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
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6
5
4
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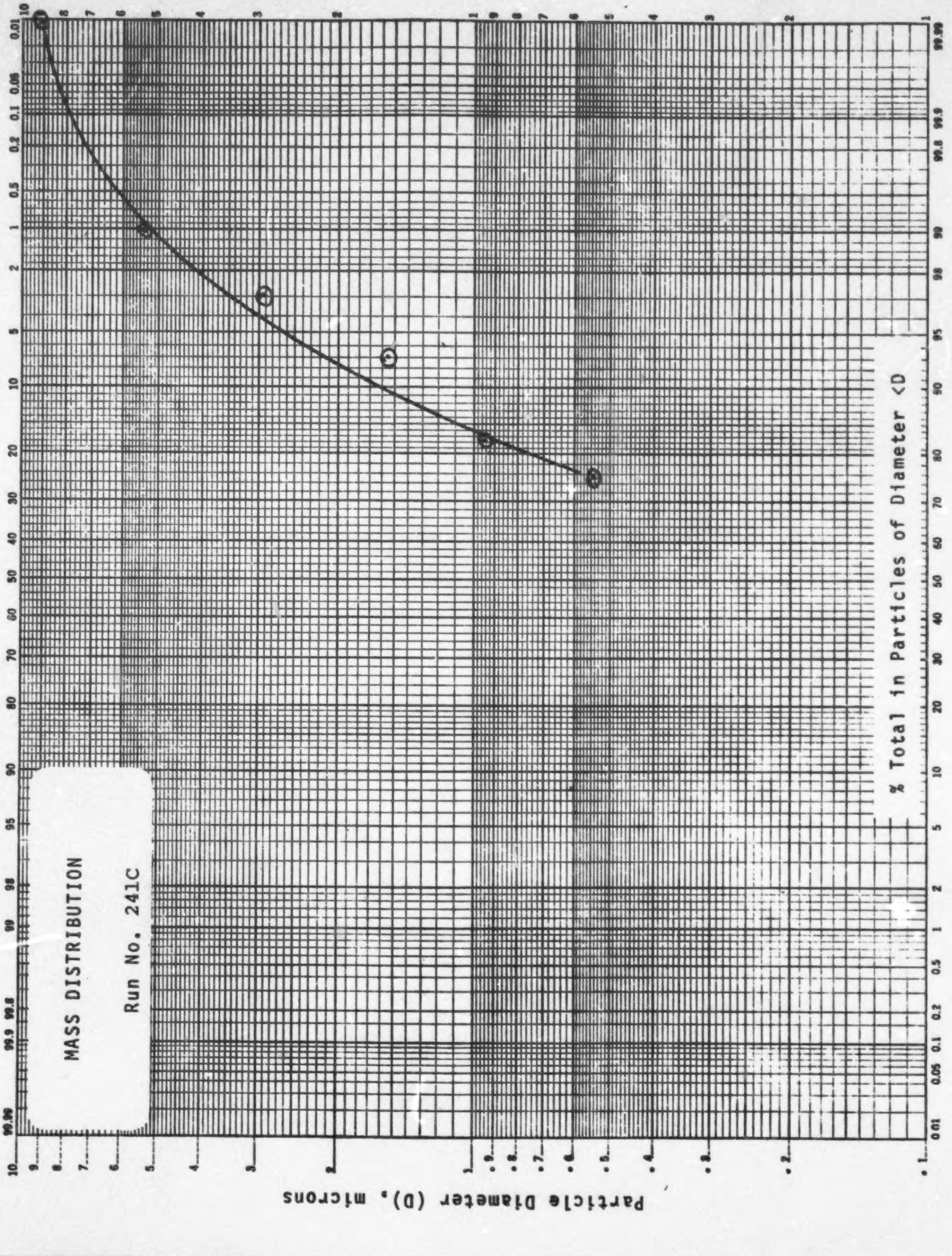
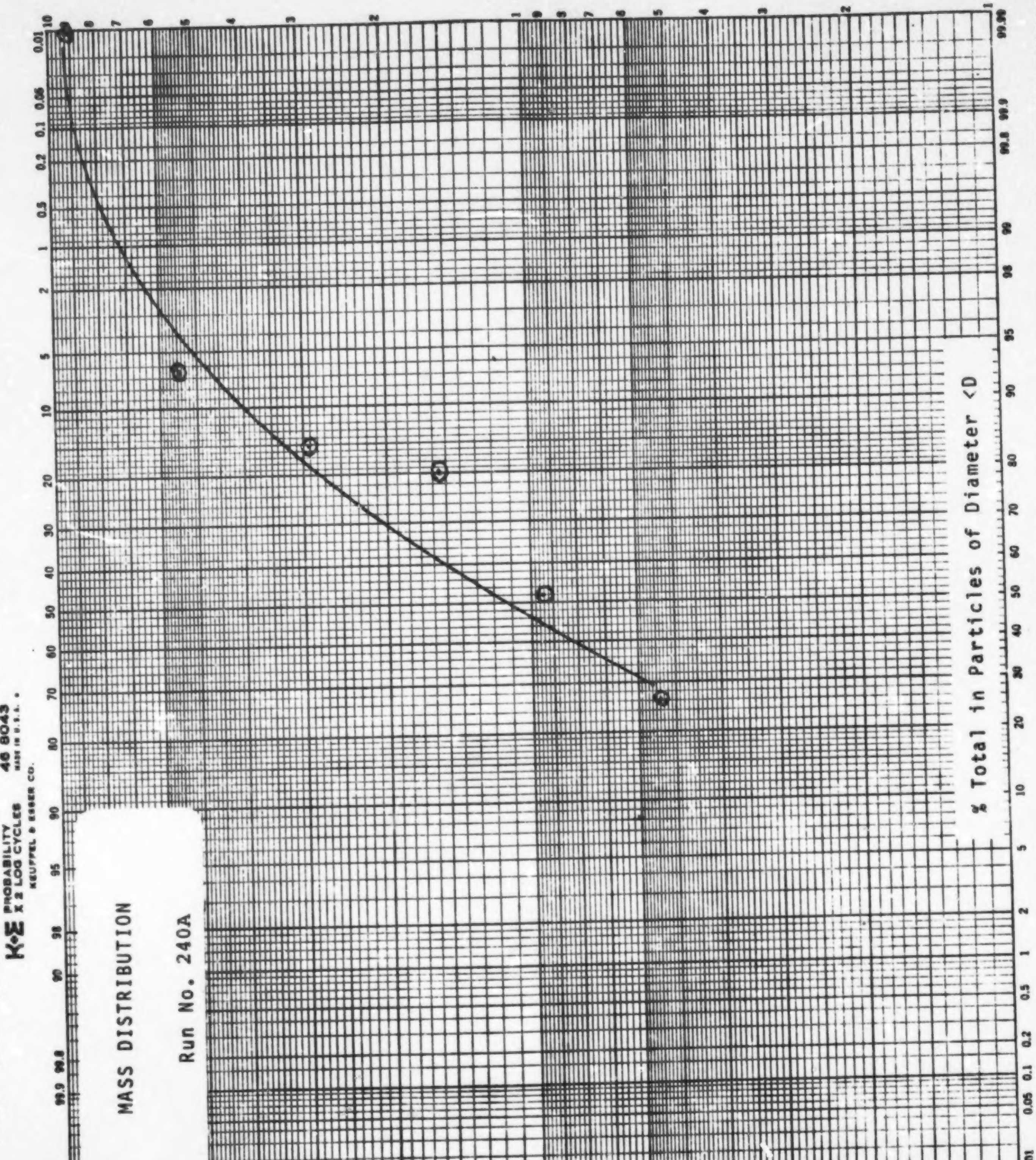
.3
.2
.1


MASS DISTRIBUTION

Run No. 241C


MASS DISTRIBUTION
Run No. 240A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
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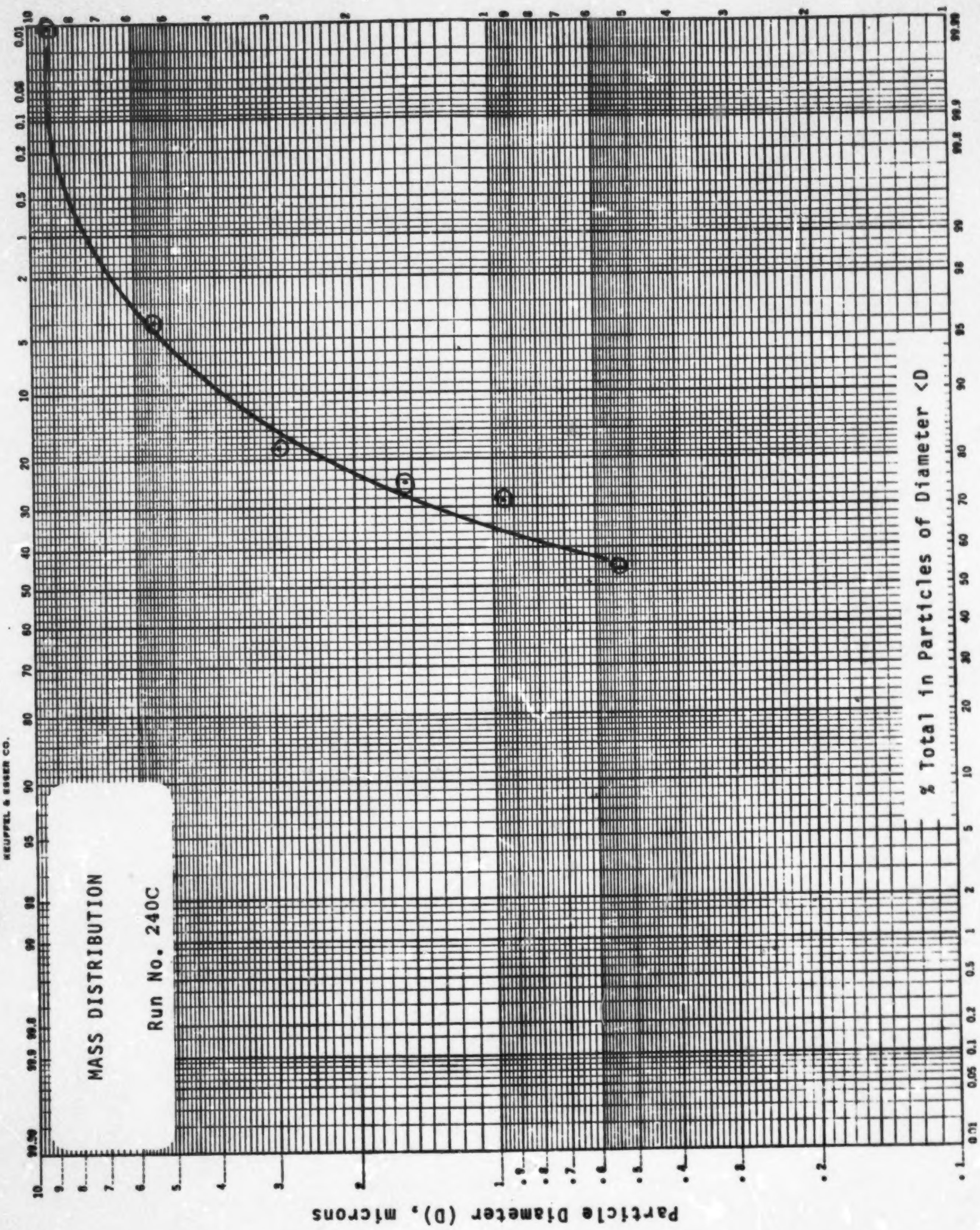
MASS DISTRIBUTION
Run No. 240C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
46 8043
MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
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70
80
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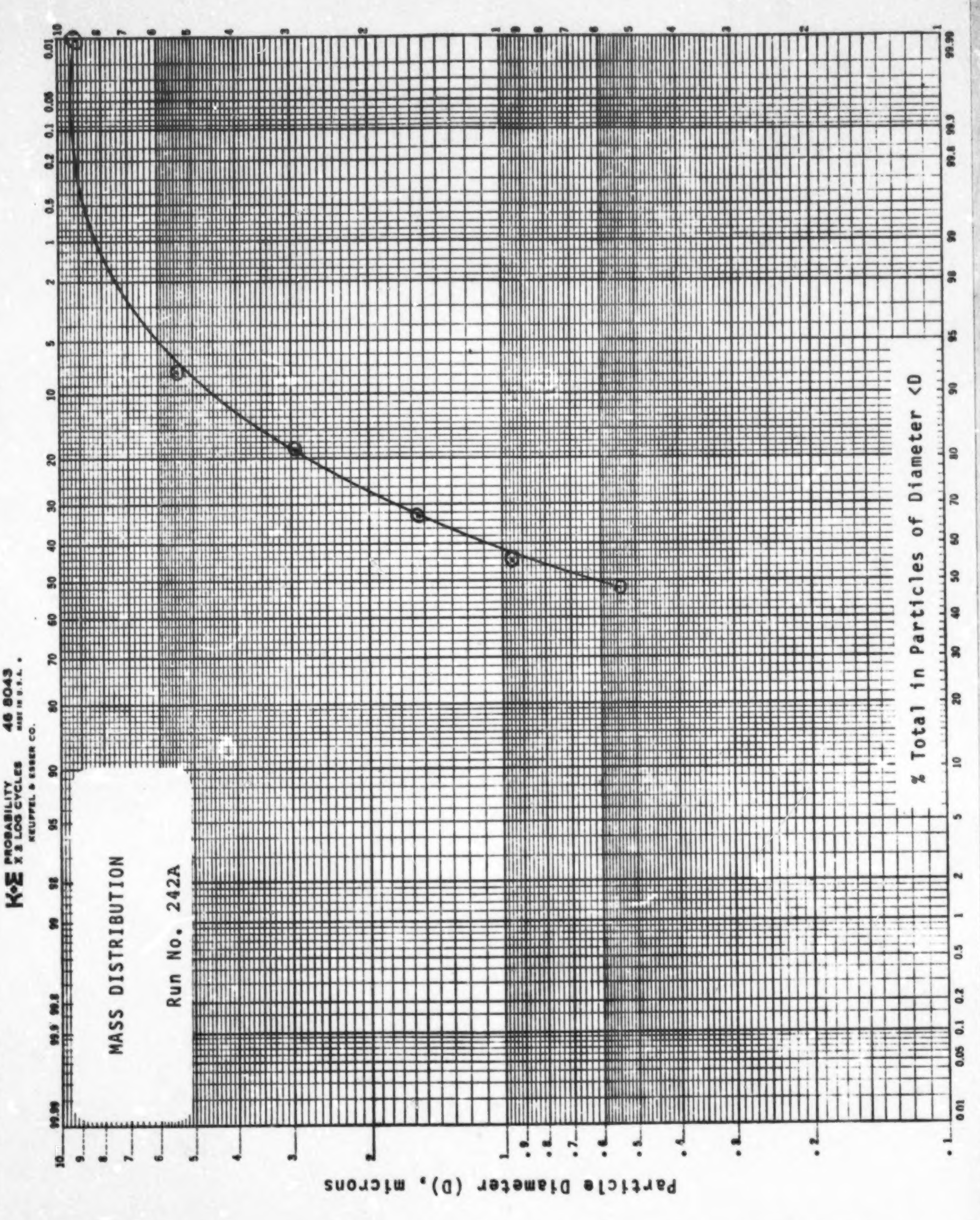
MASS DISTRIBUTION
Run No. 242A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
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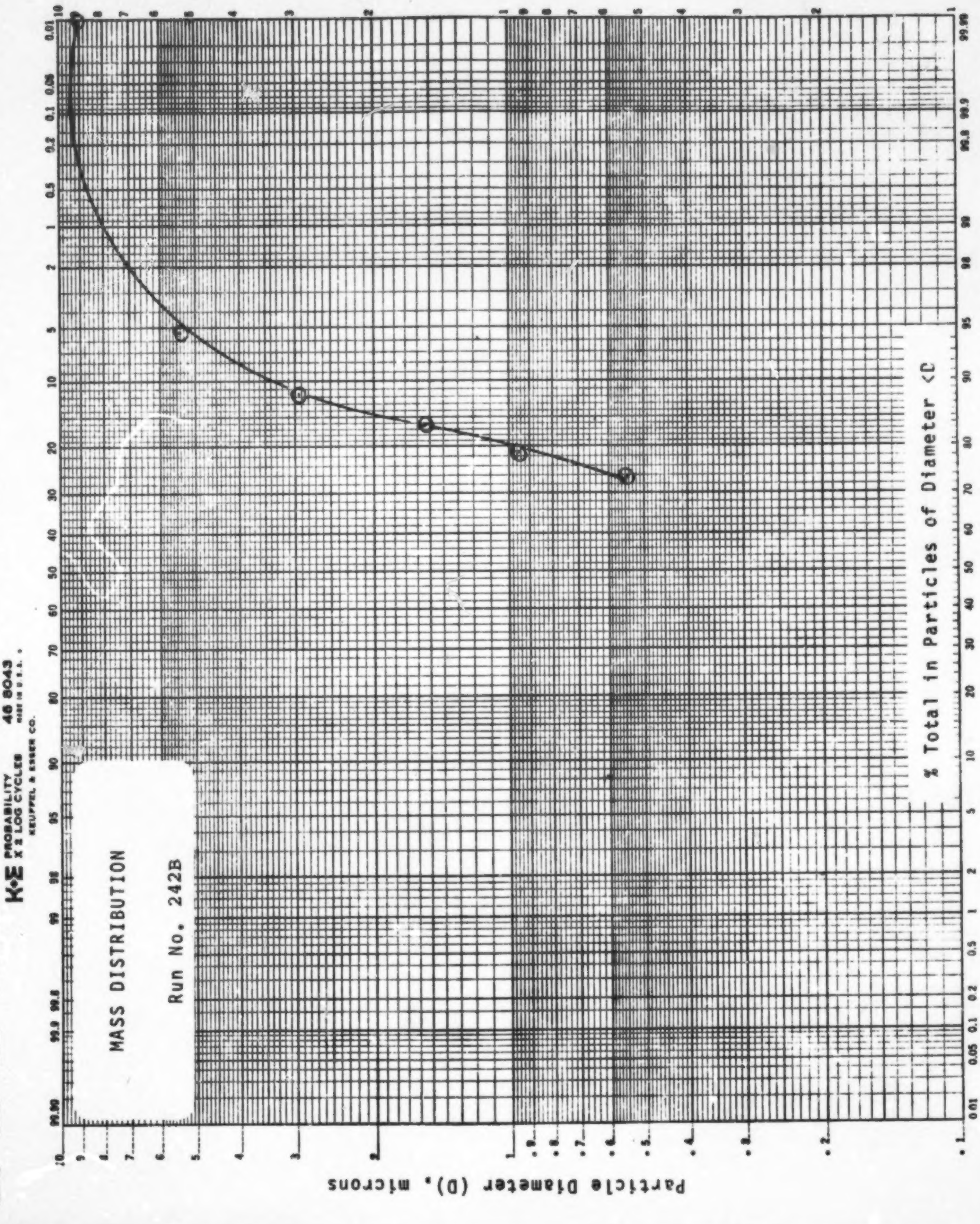
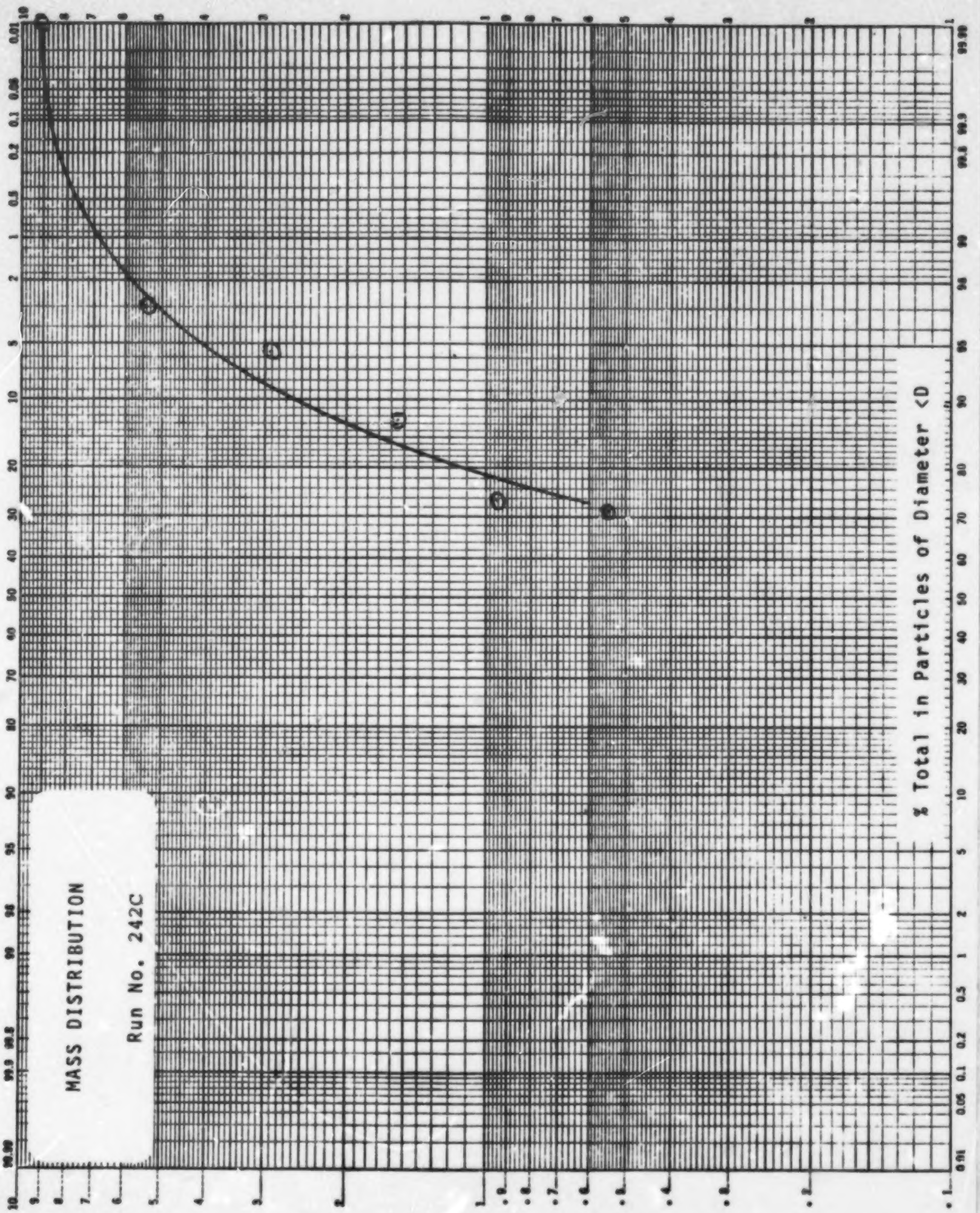

MASS DISTRIBUTION
Run No. 242B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K•E PROBABILITY X 2 LOG CYCLES 46 8043 KEUFFEL & ESSER CO.
0.01 0.05 0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99
99.99 99.9 99.8 99 98 95 90 80 70 60 50 40 30 20 10 5 2 1 0.5 0.2 0.1 0.05 0.01
10 9 8 7 6 5 4 3 2 1 .9 .8 .7 .6 .5 .4 .3 .2 .1


MASS DISTRIBUTION
Run No. 242C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
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0.1
0.2
0.5
1
2
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30
40
50
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70
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95
98
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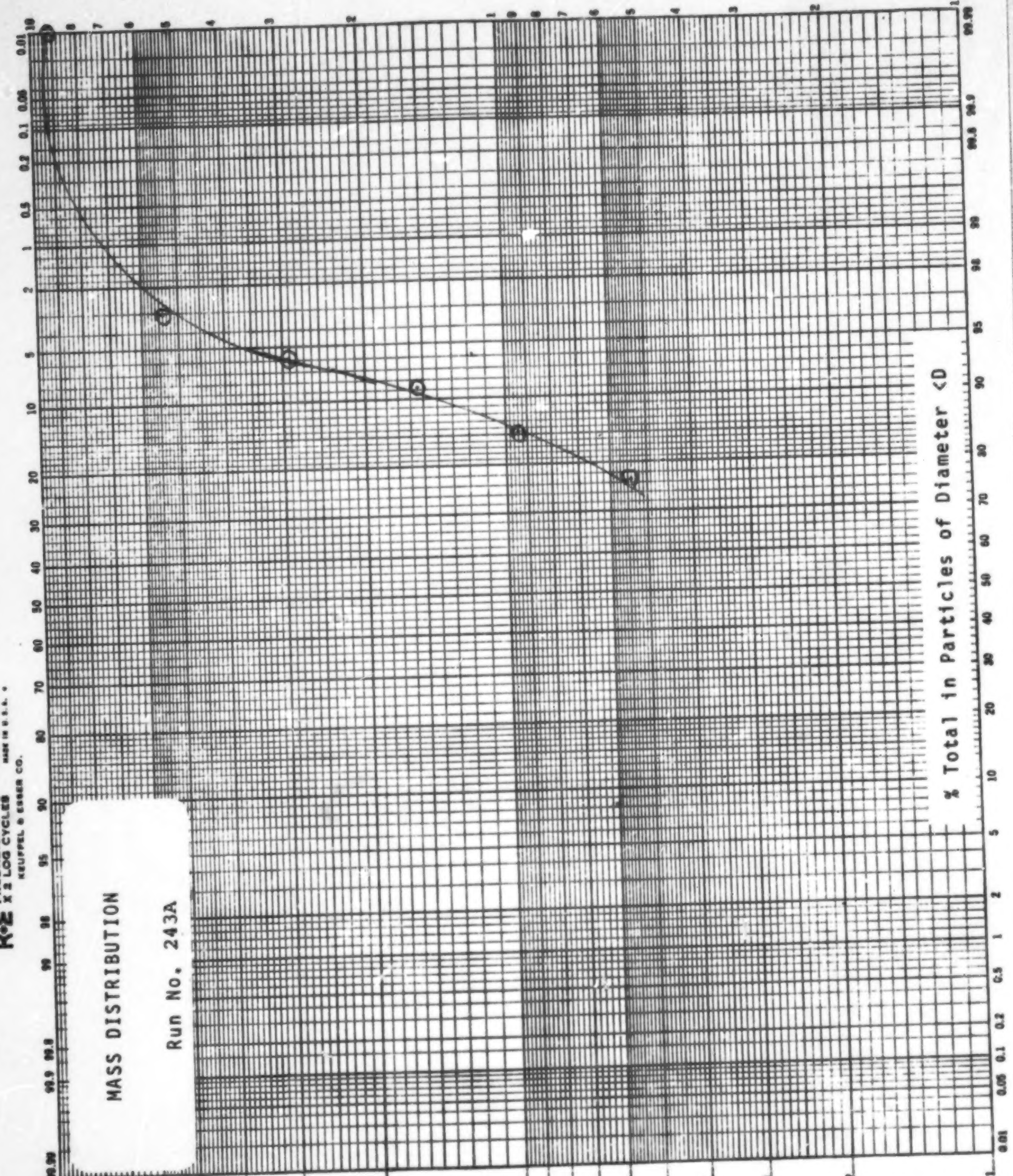
MASS DISTRIBUTION
Run No. 243A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
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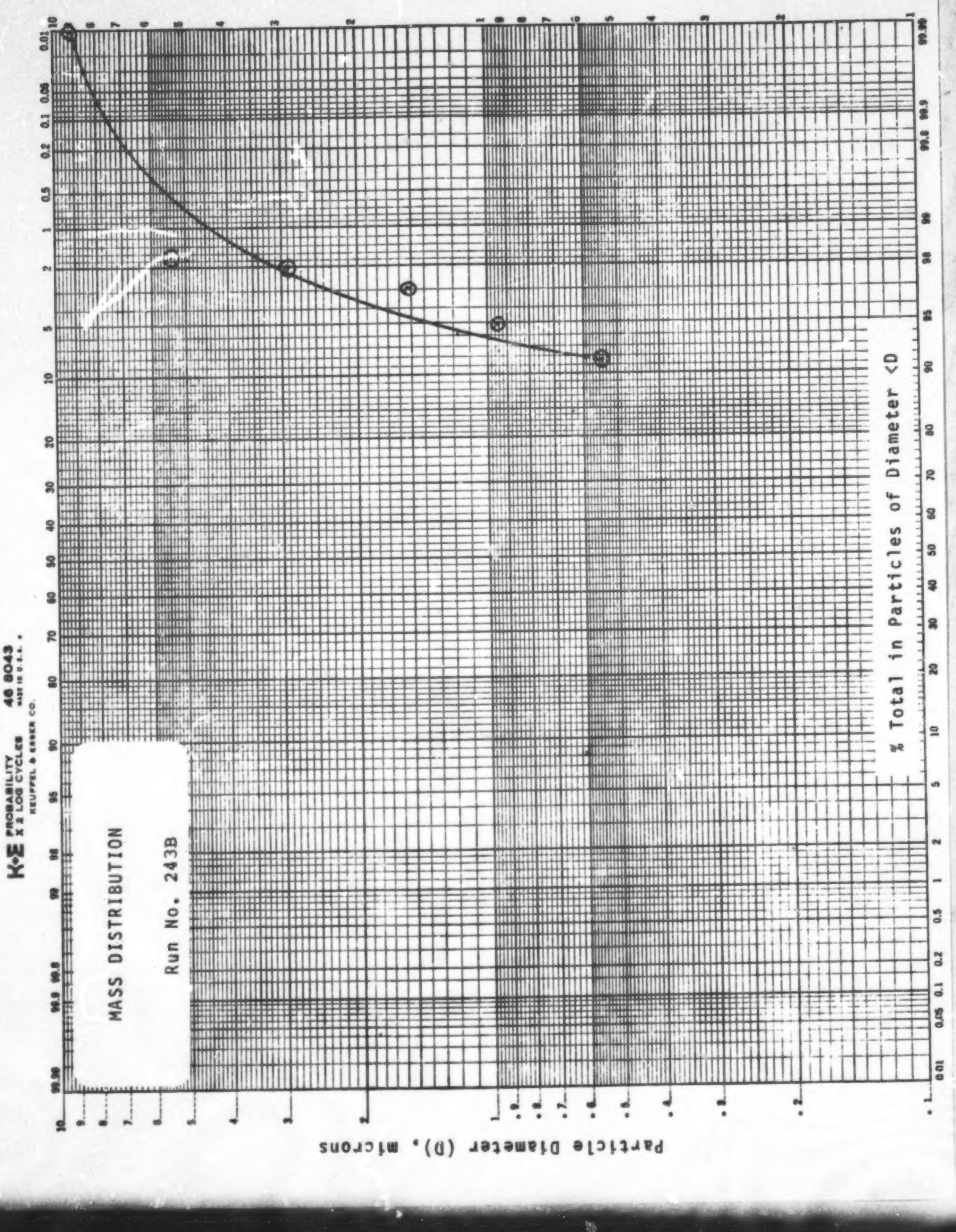
MASS DISTRIBUTION
Run No. 243B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
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99.8
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99.99
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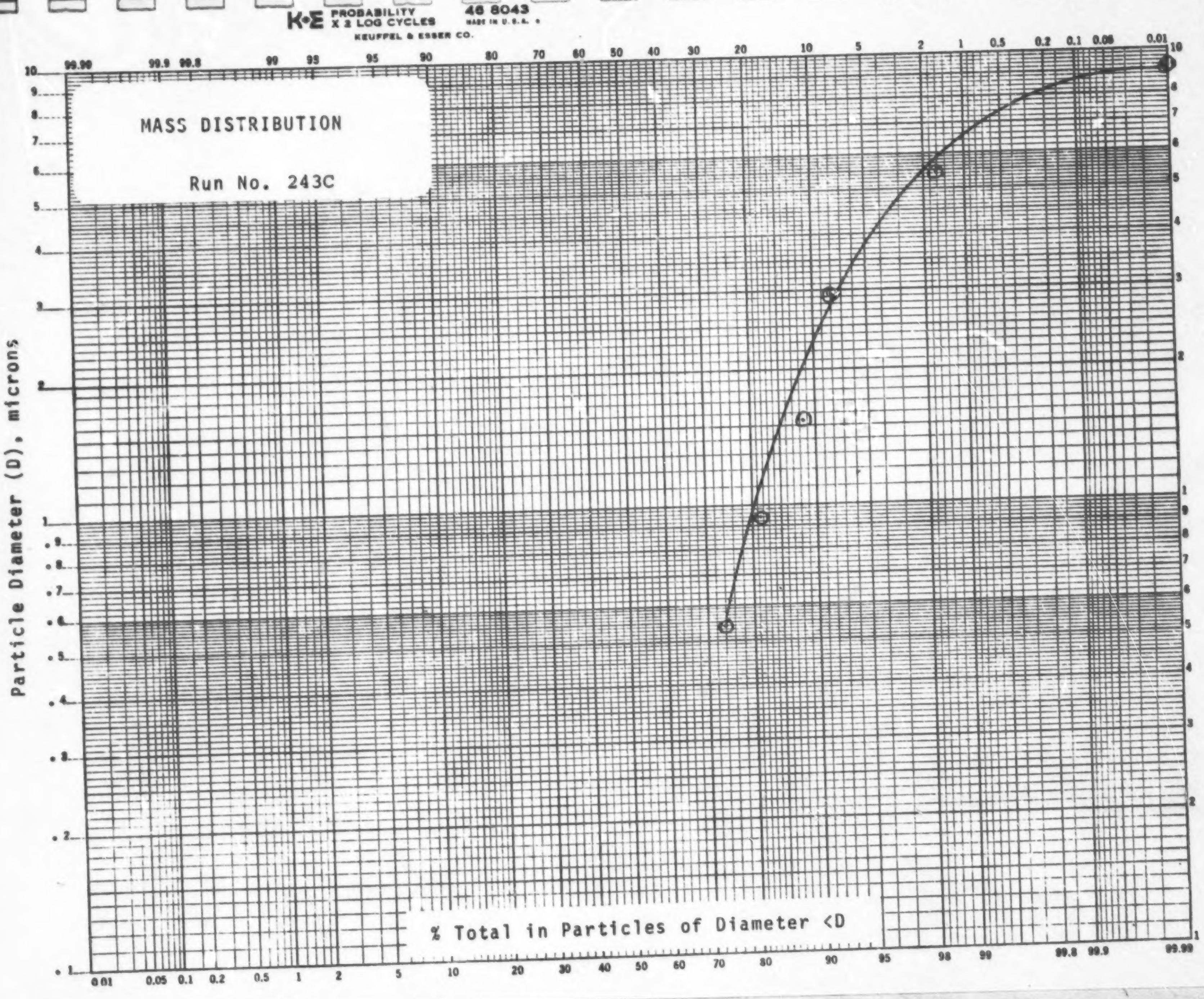
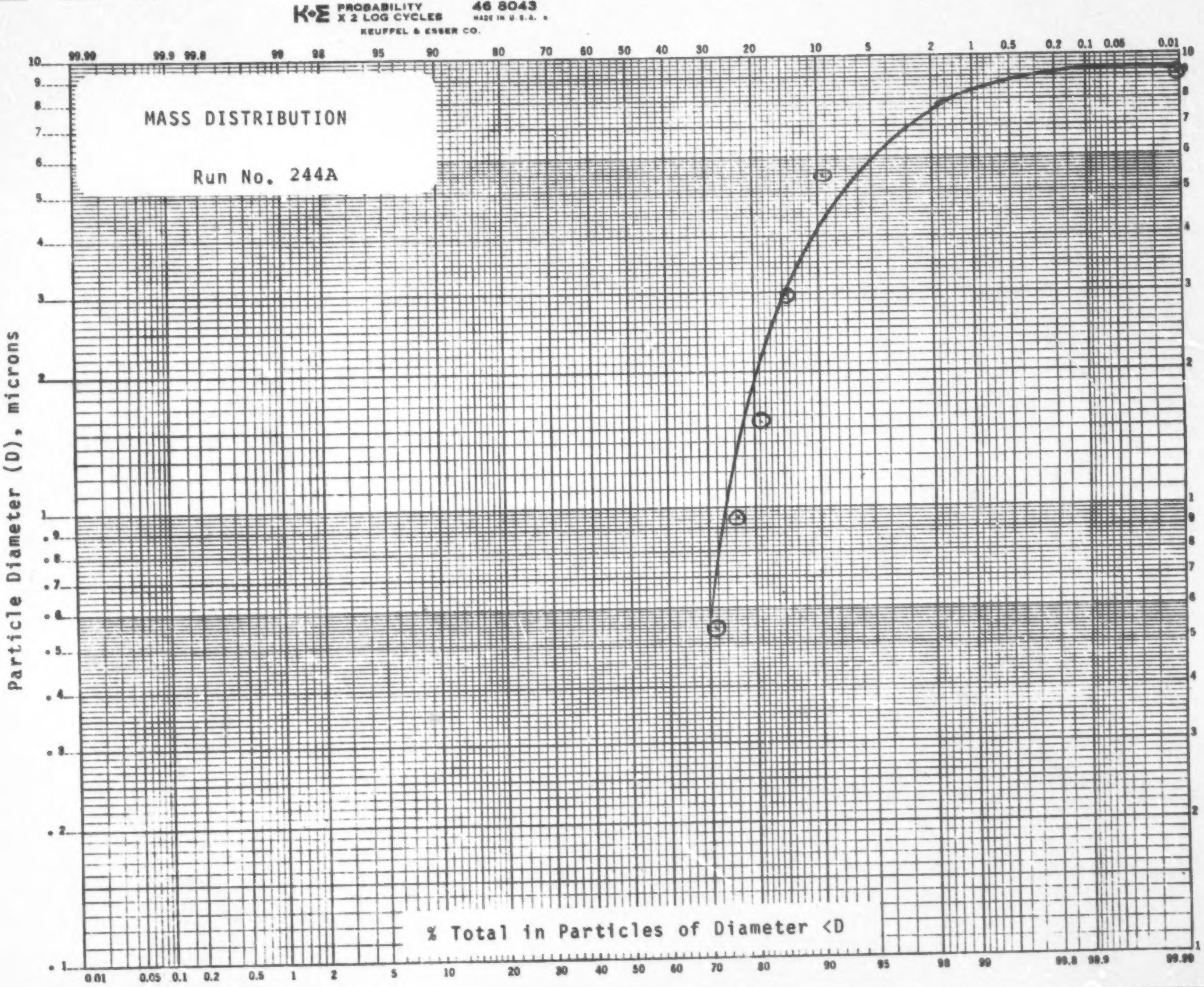


MASS DISTRIBUTION

Run No. 243C


K+E PROBABILITY X 2 LOG CYCLES KEUFFEL & ESSER CO. 46 8043 MADE IN U.S.A.
MASS DISTRIBUTION
Run No. 244A
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
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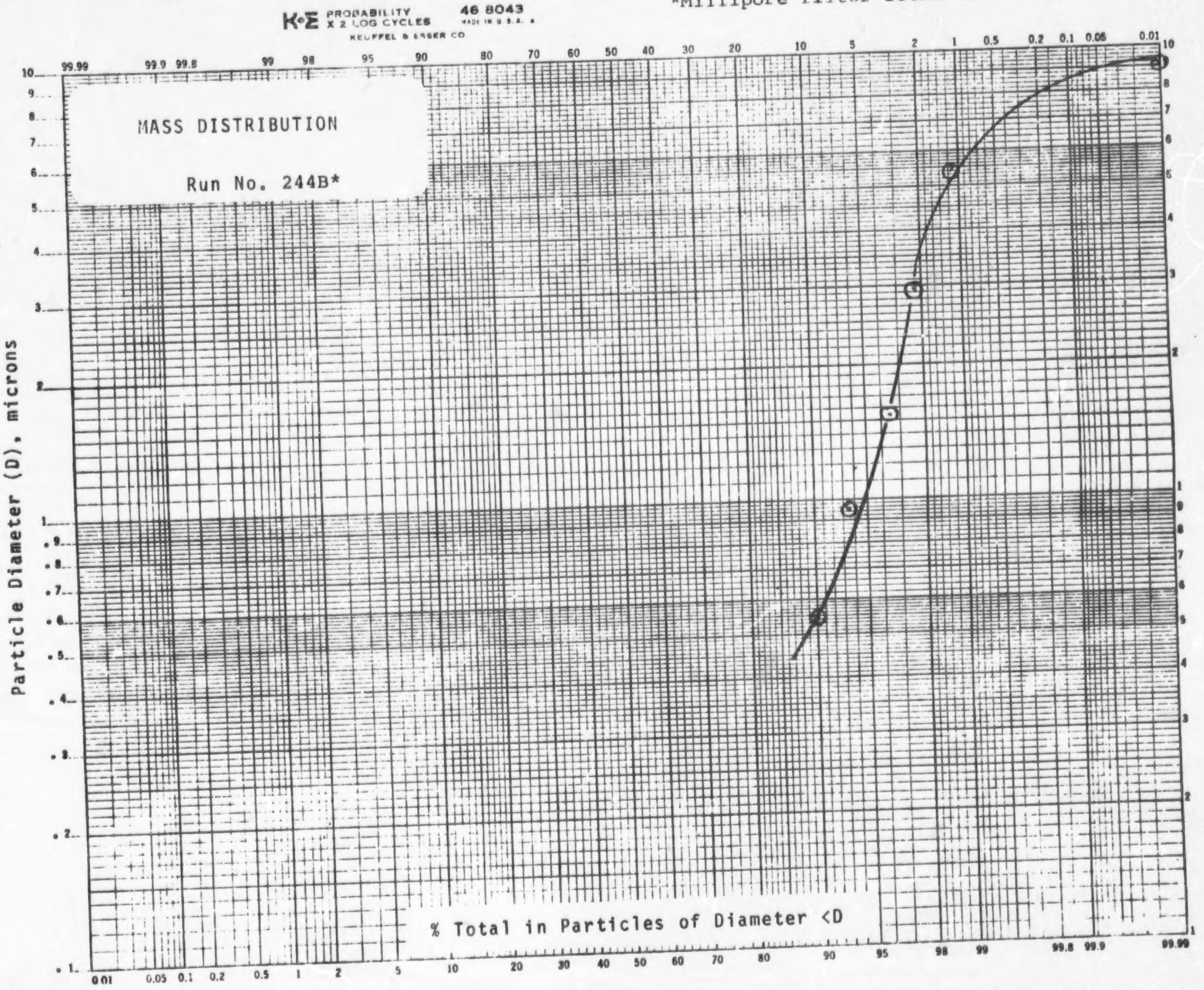
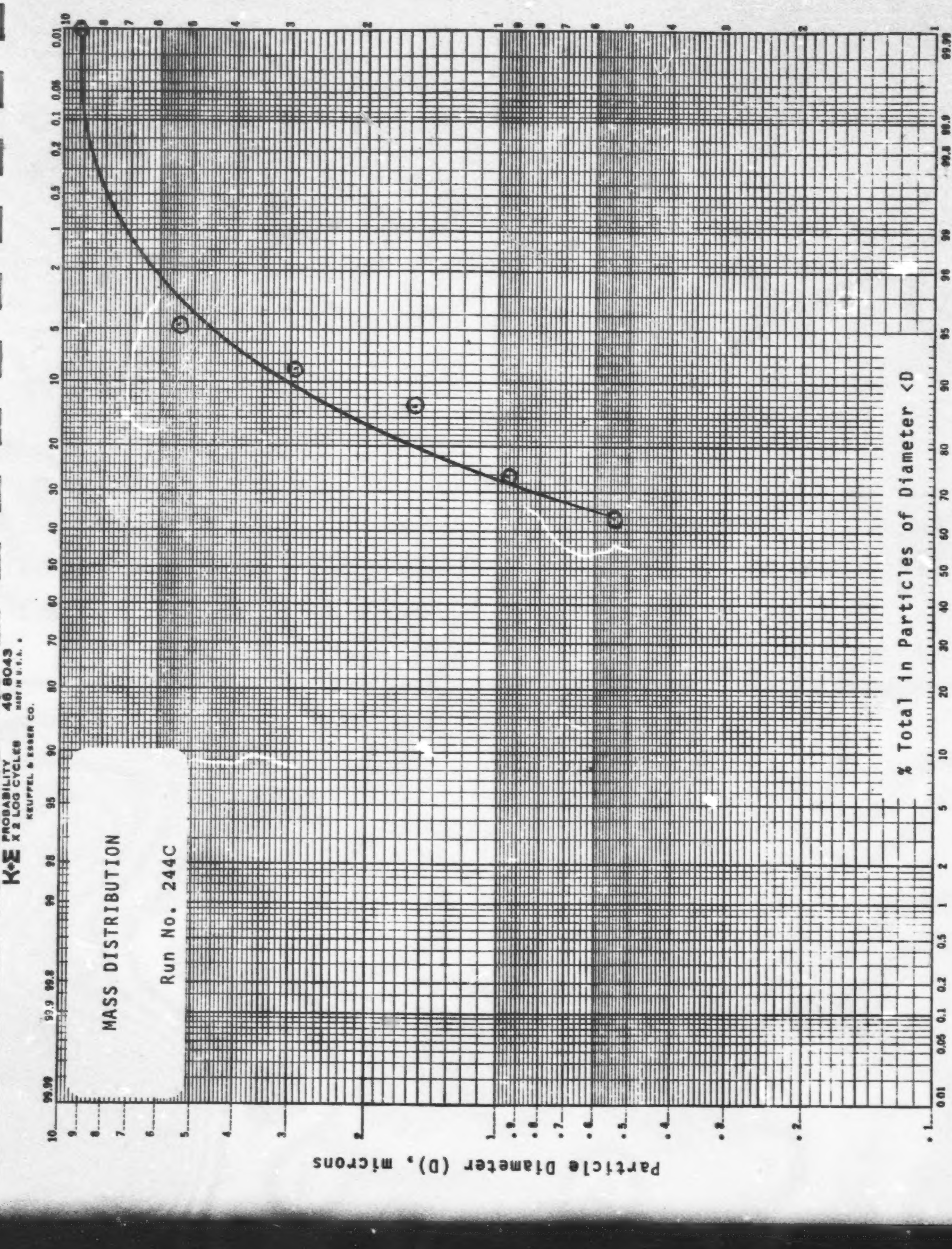
*Millipore filter seems out of line High




MASS DISTRIBUTION
Run No. 244C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K•E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
0.01
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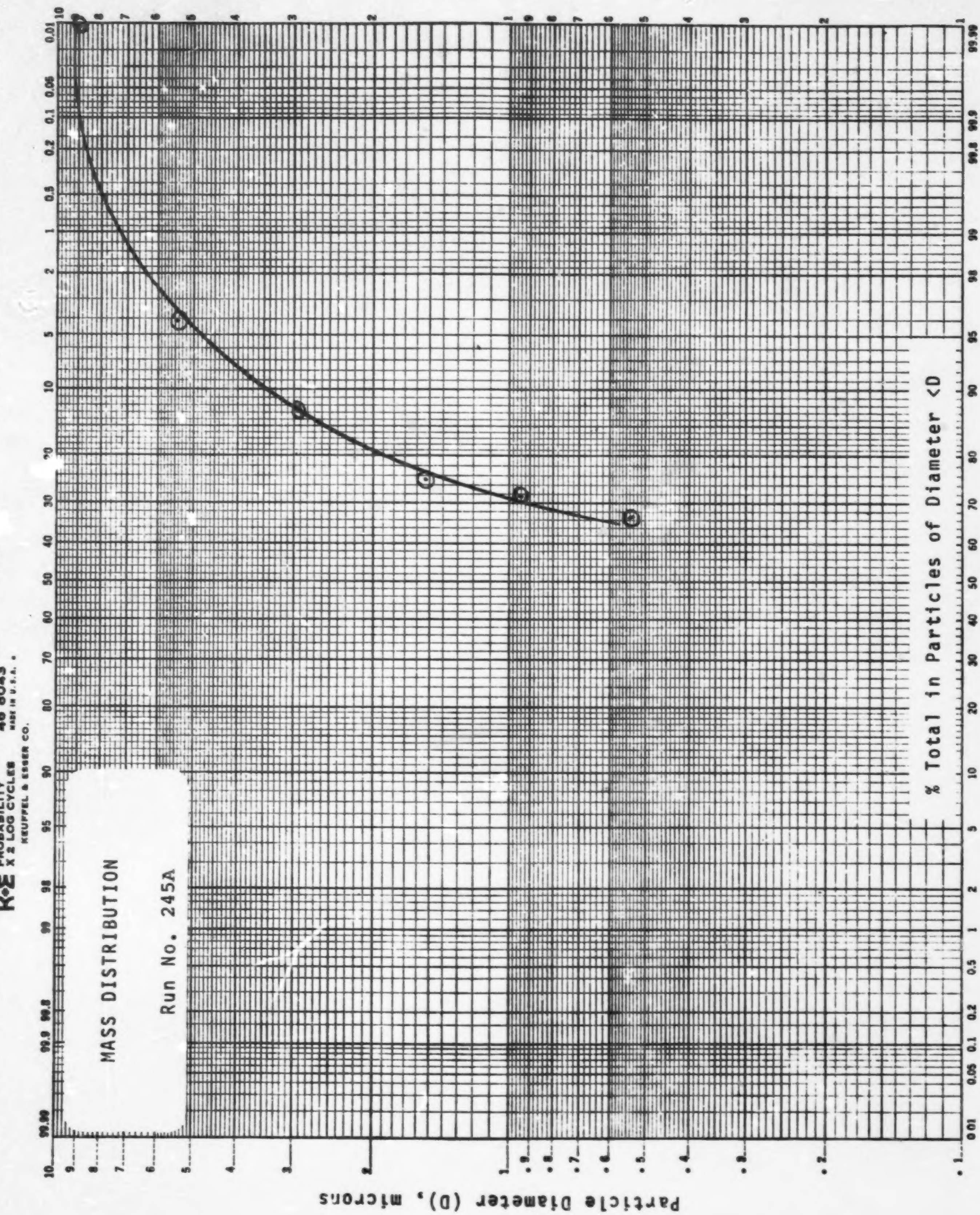
MASS DISTRIBUTION
Run No. 245A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
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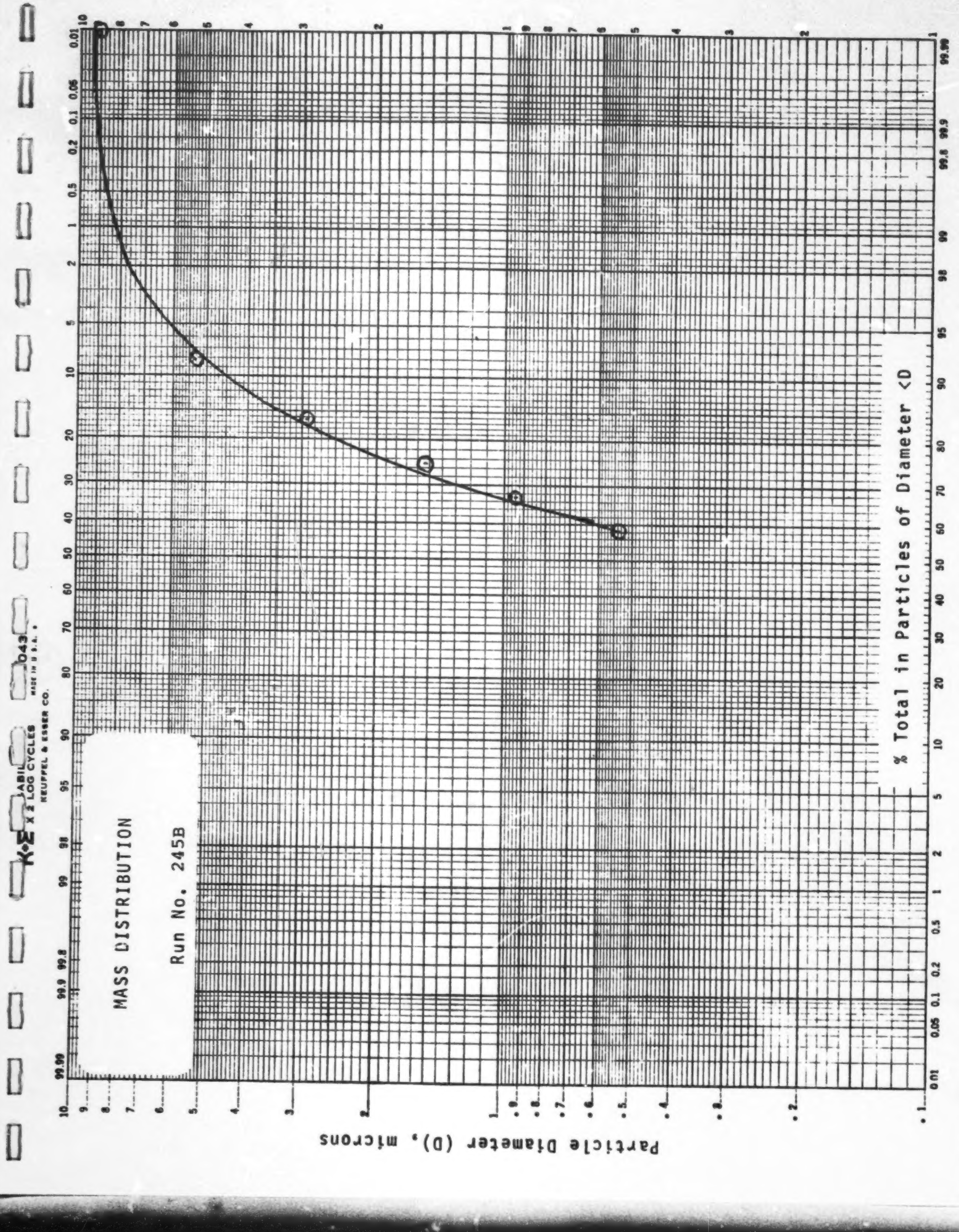
99.99
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
MADE IN U.S.A.


MASS DISTRIBUTION
Run No. 245B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E X 2 LOG CYCLES
KEUFFEL & ESSER CO.
MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
1
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99.8
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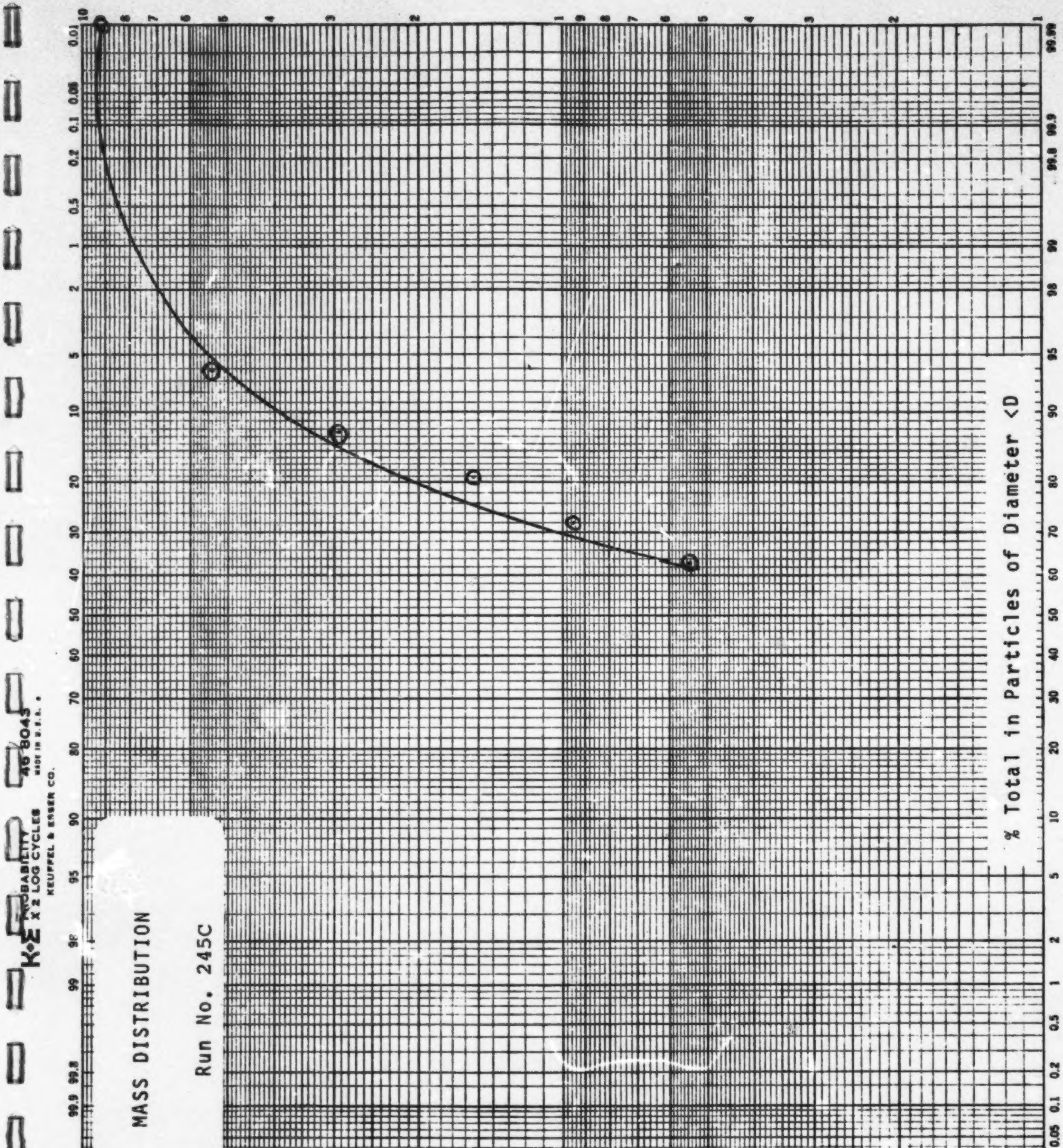
MASS DISTRIBUTION
Run No. 245C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043 MADE IN U.S.A. KEUFFEL & ESSER CO.
0.01
0.05
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1
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70
80
90
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99.8
99.9
99.99
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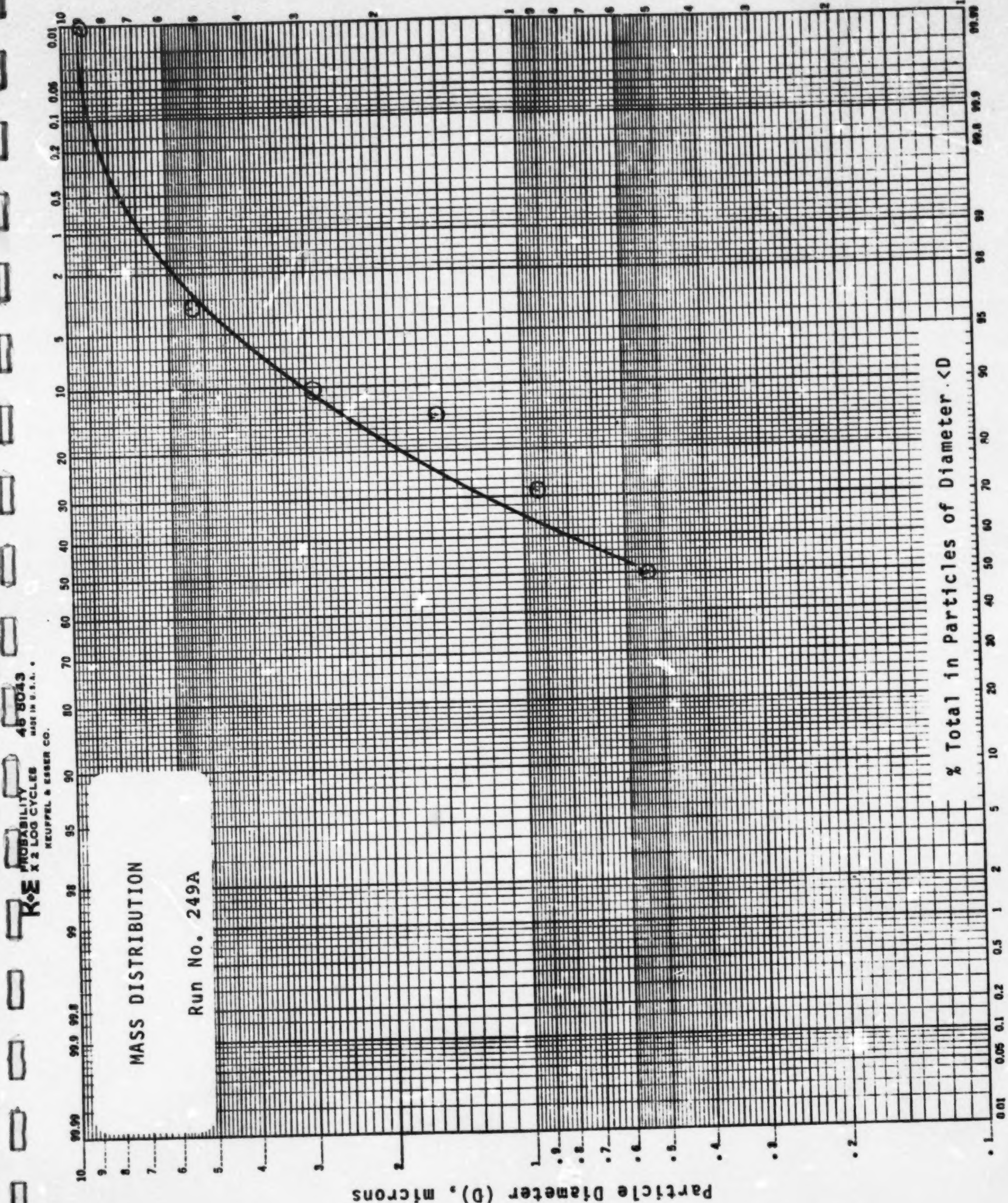
MASS DISTRIBUTION
Run No. 249A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO. MADE IN U.S.A.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
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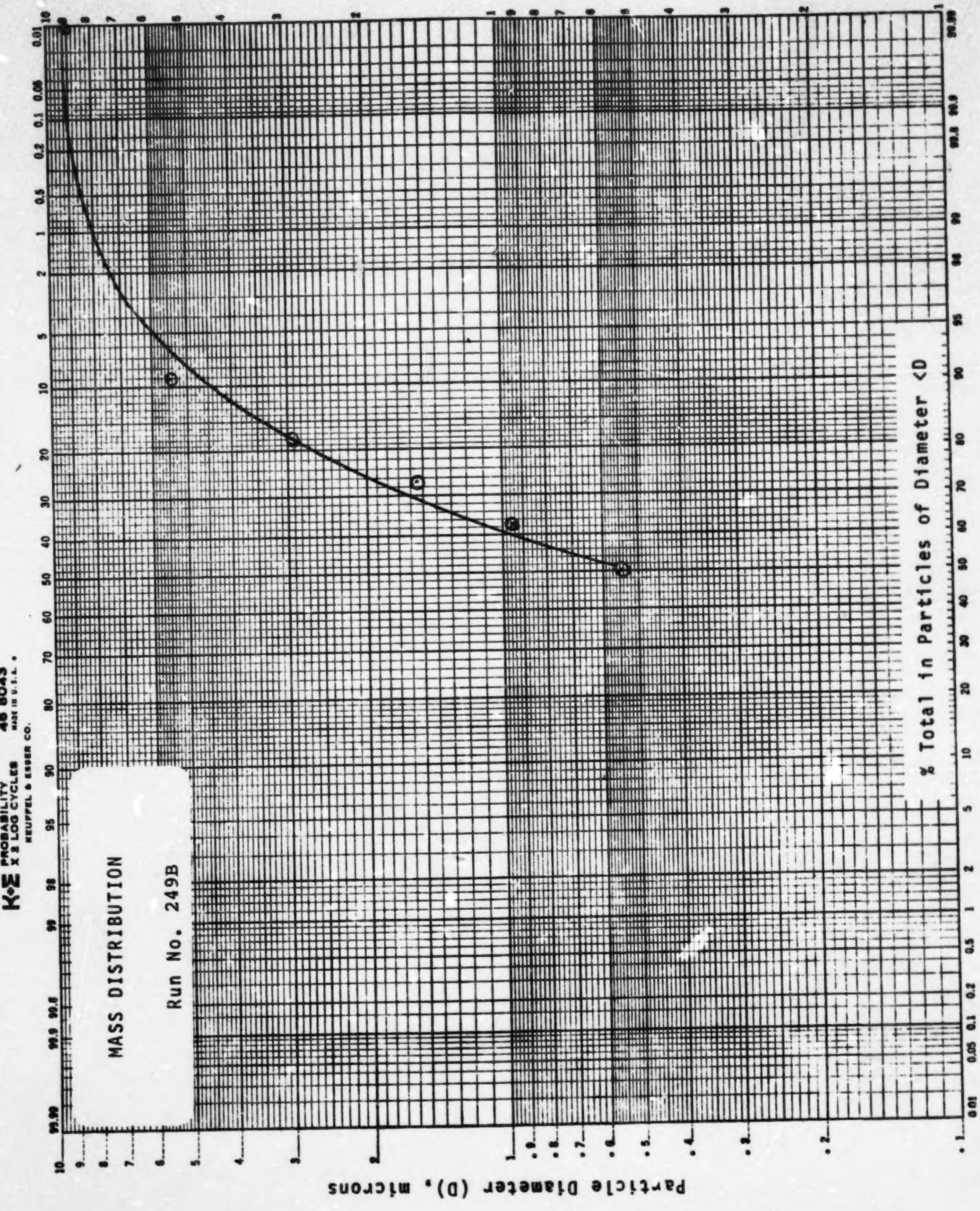
MASS DISTRIBUTION
Run No. 249B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
10
9
8
7
6
5
4
3
2
1
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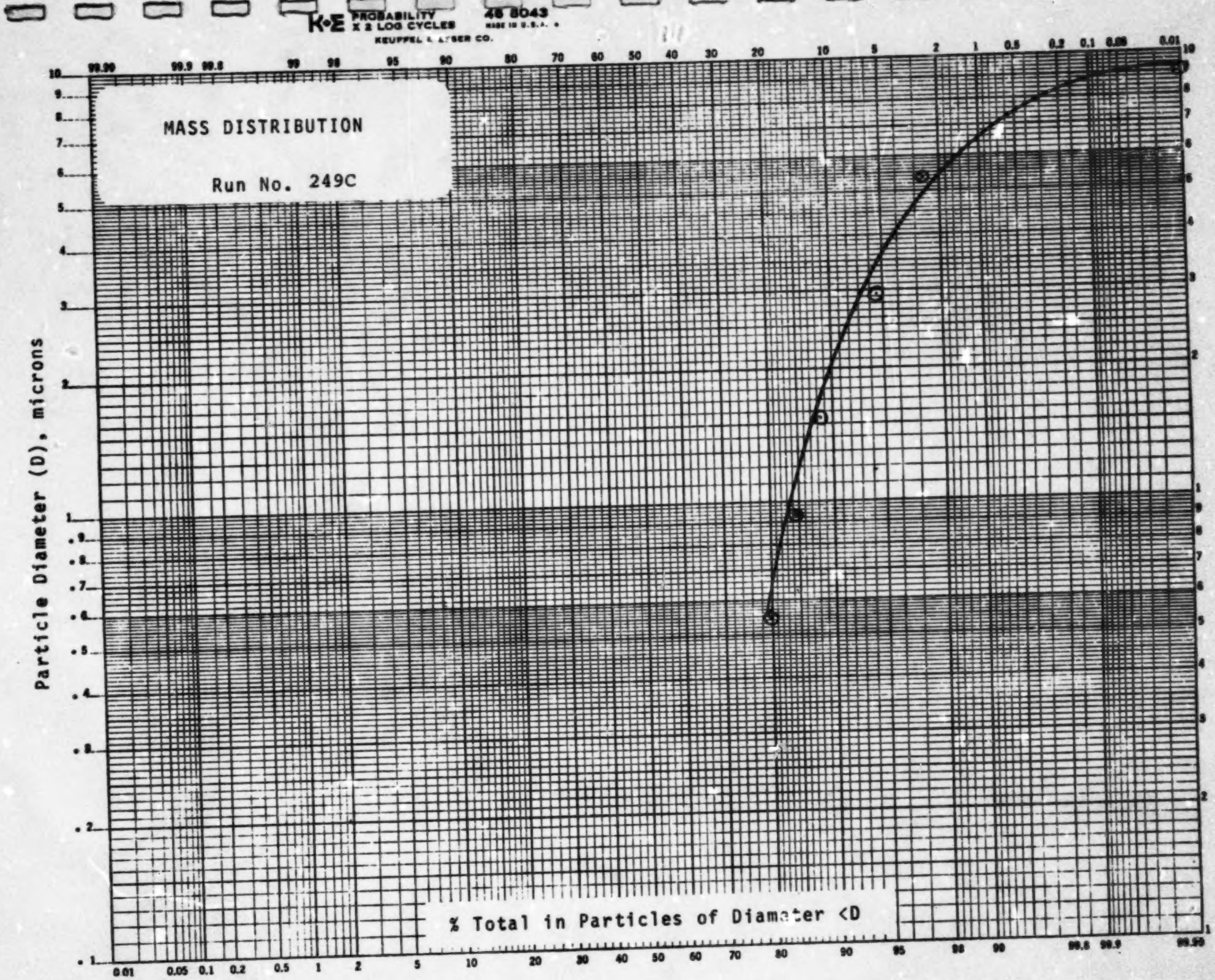
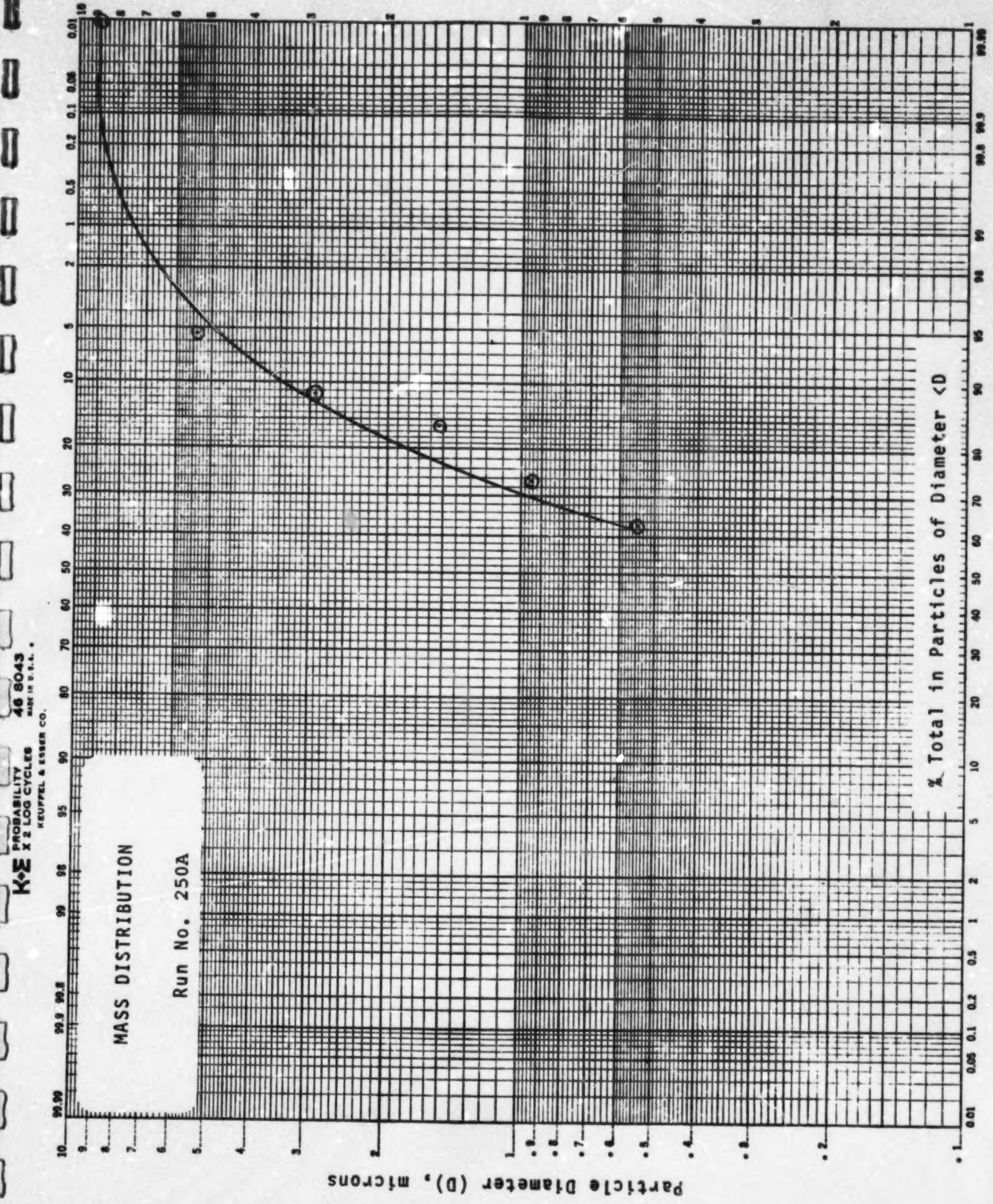
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
K&E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.



MASS DISTRIBUTION

Run No. 249C


MASS DISTRIBUTION
Run No. 250A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K&E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
MADE IN U.S.A.
0.01
0.05
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99.8
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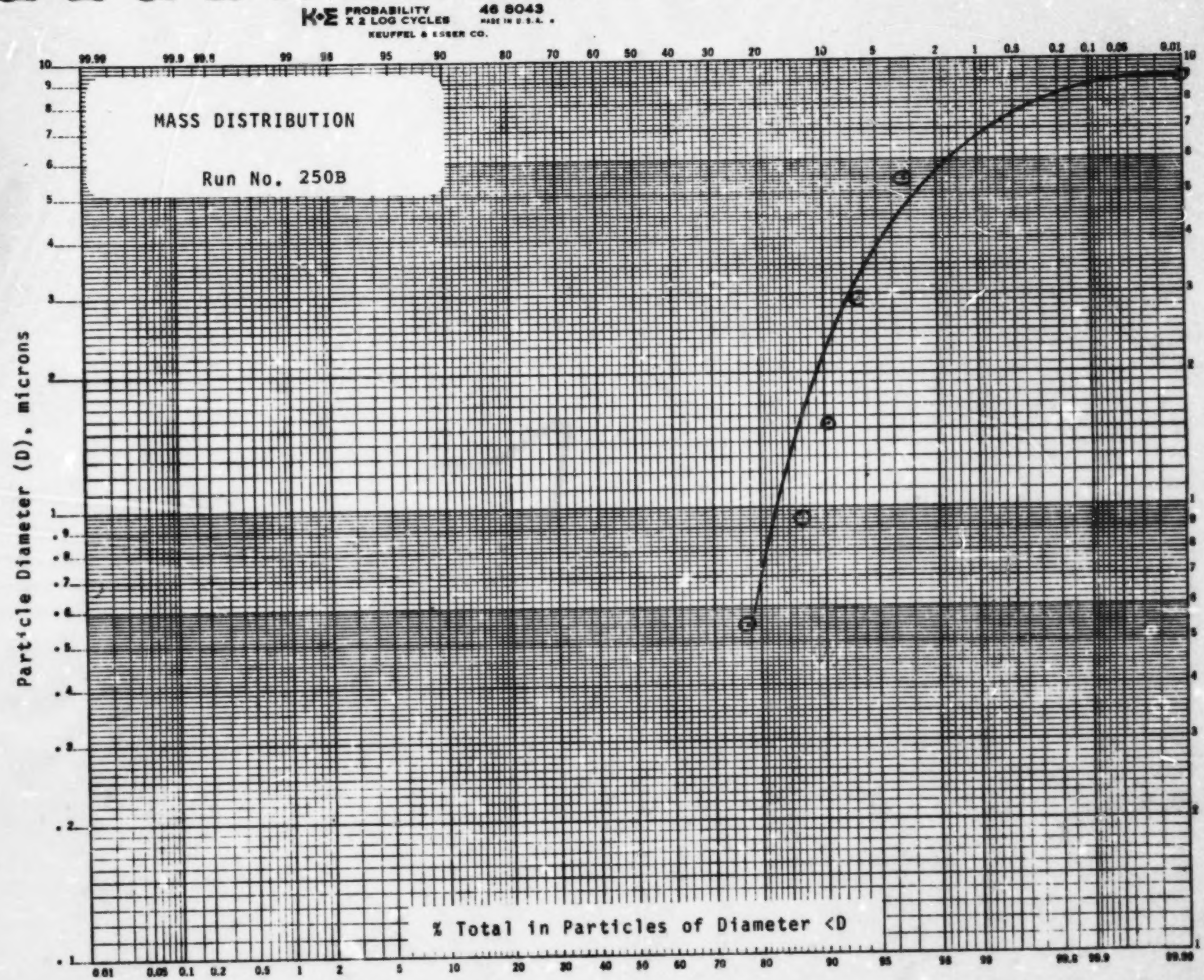
K•E PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
46 8043
MADE IN U.S.A.
MASS DISTRIBUTION
Run No. 250B
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
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60
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0.5
0.2
0.1
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0.01
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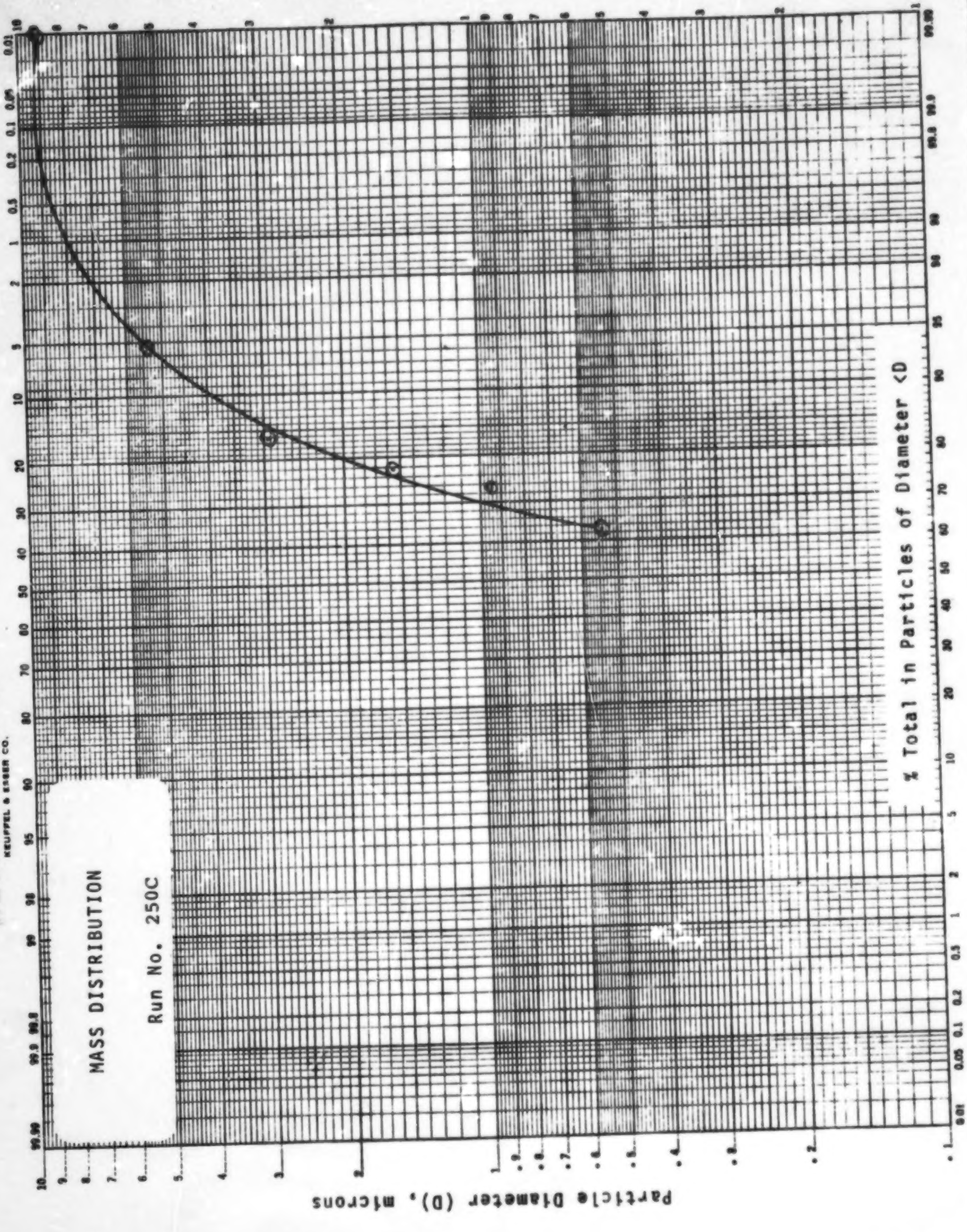
MASS DISTRIBUTION
Run No. 250C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
0.01
0.05
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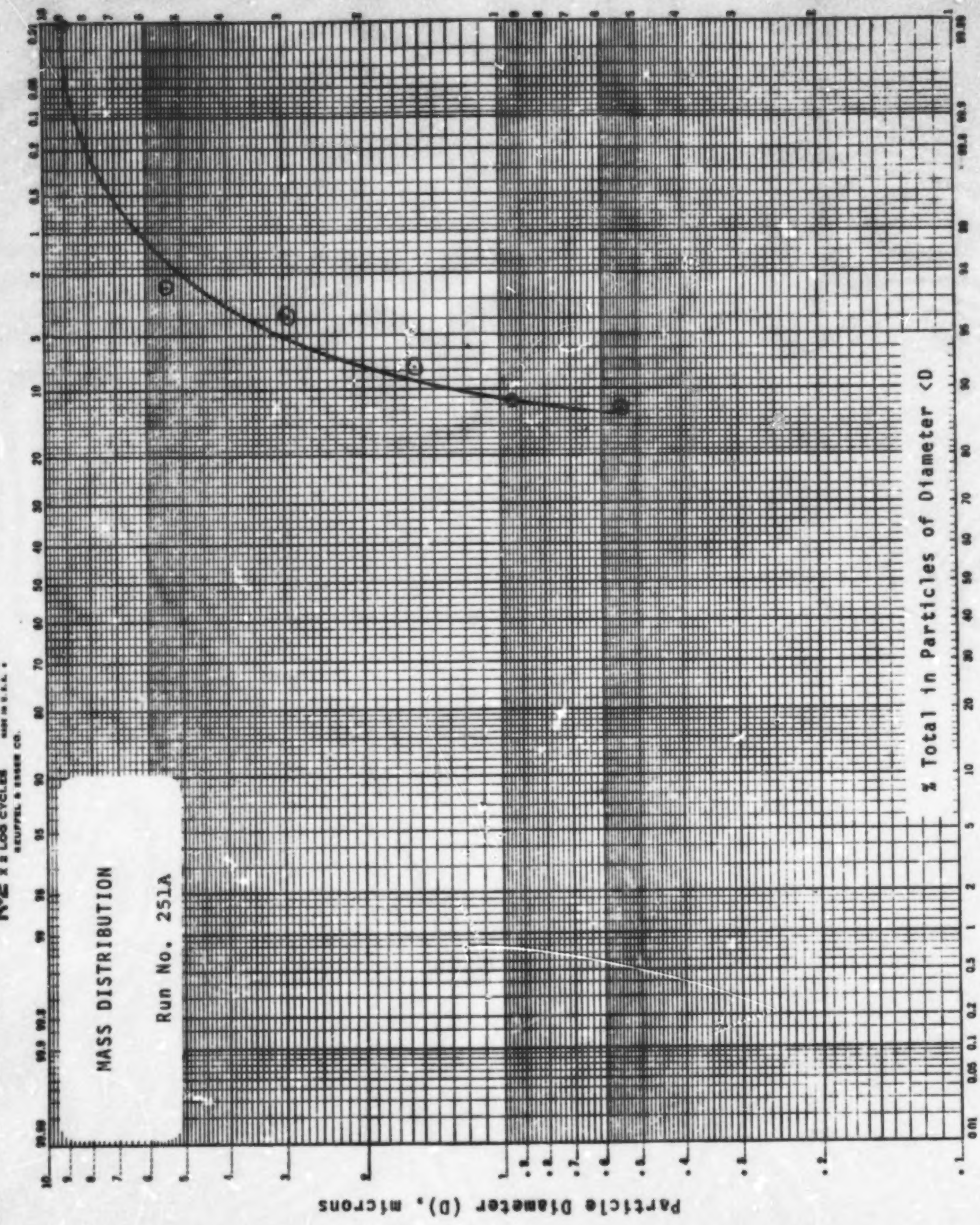
MASS DISTRIBUTION
Run No. 251A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
99.99
99.9 99.8
99
98
95
90
80
70
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0.5
0.2
0.1
0.05
0.01
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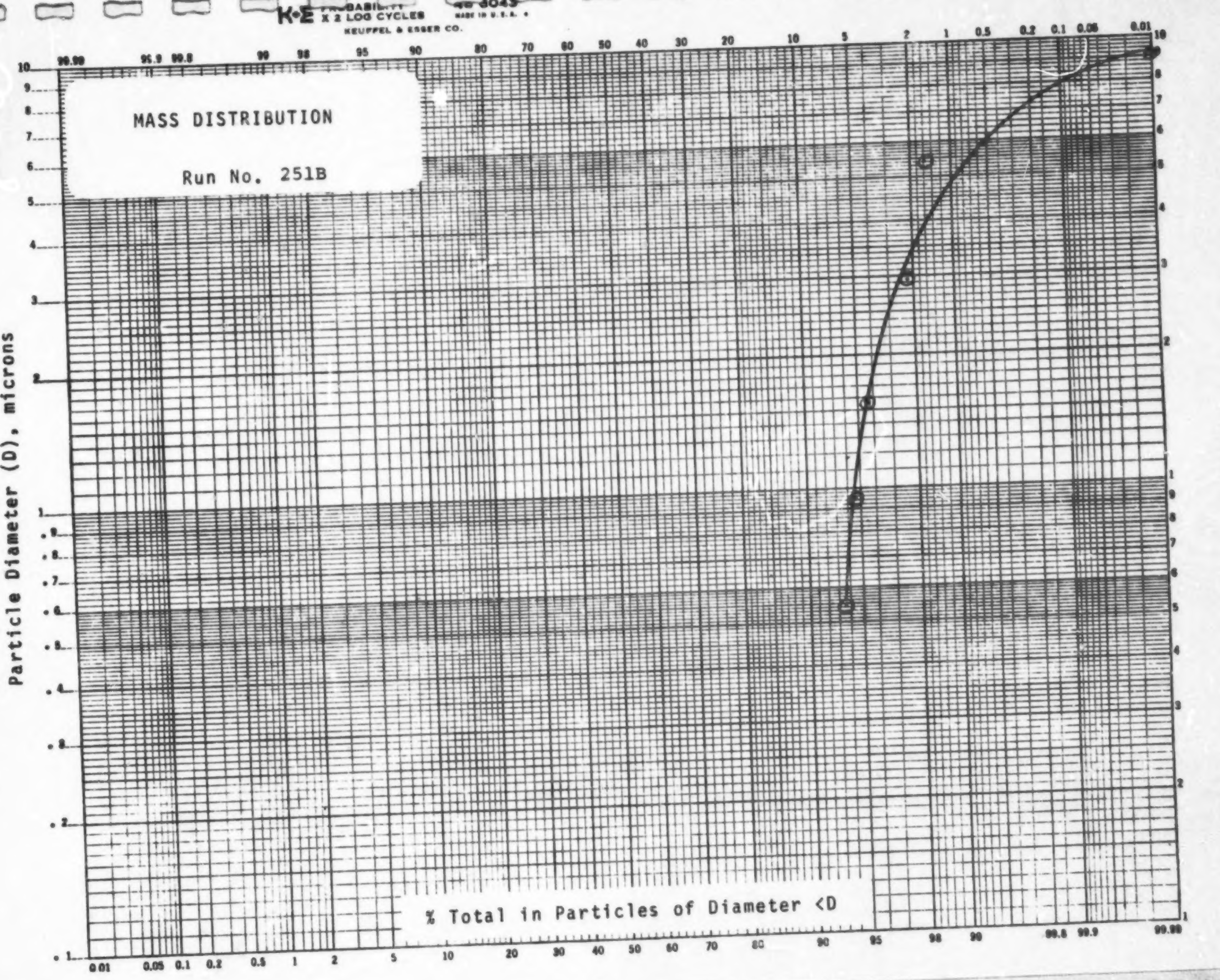
K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 251B
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
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98
95
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0.01
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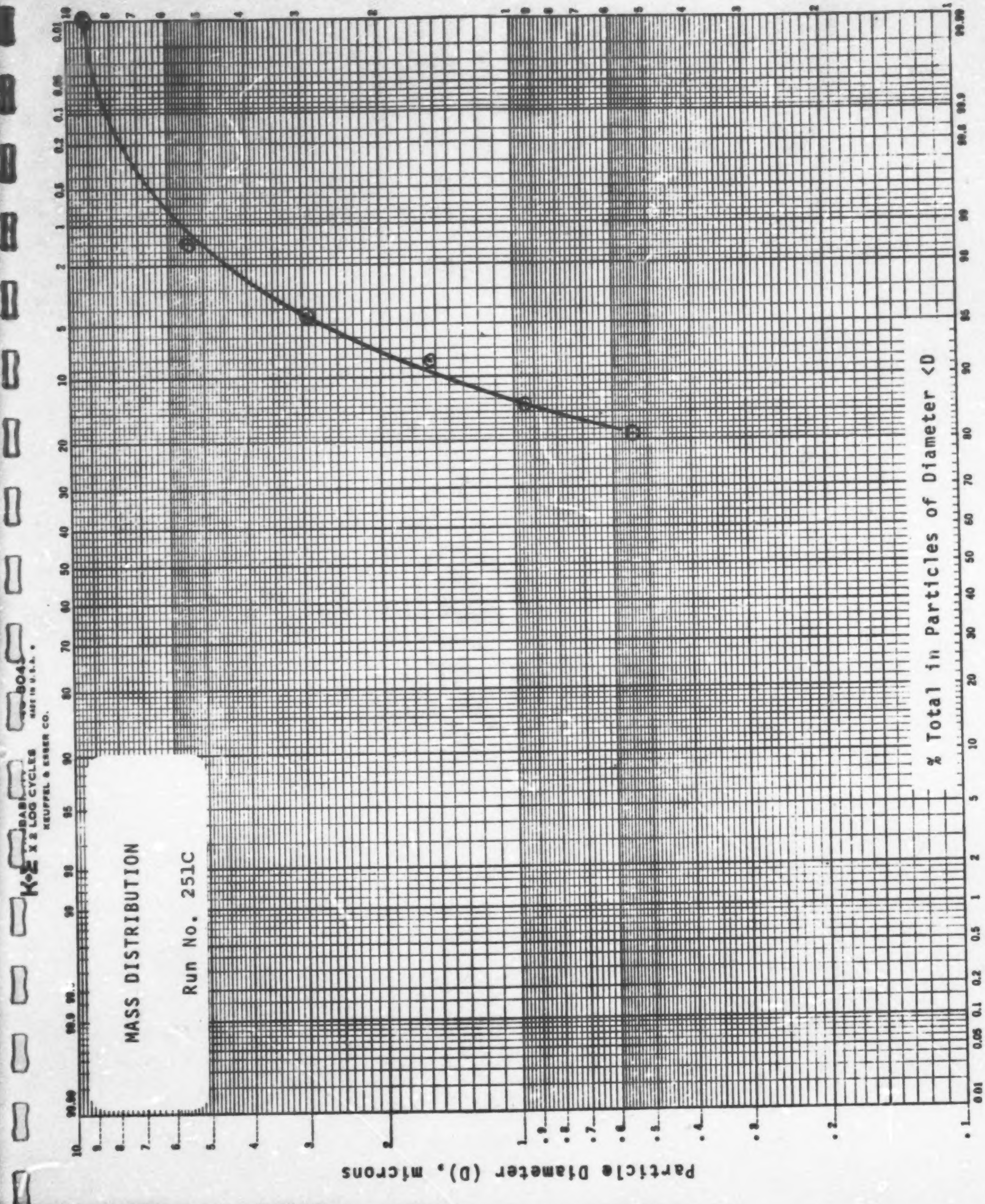
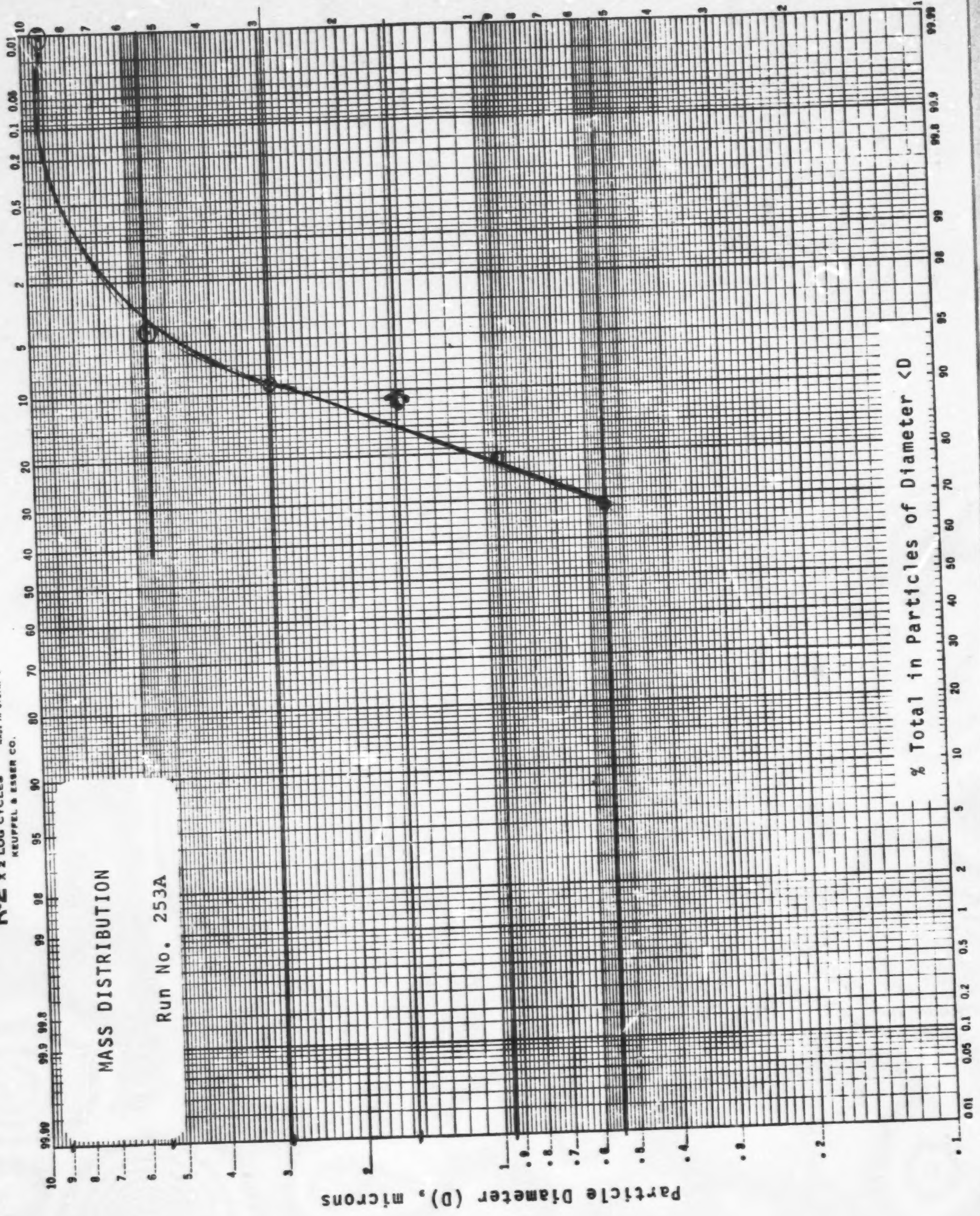
99.99


MASS DISTRIBUTION

Run No. 251C


MASS DISTRIBUTION
Run No. 253A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
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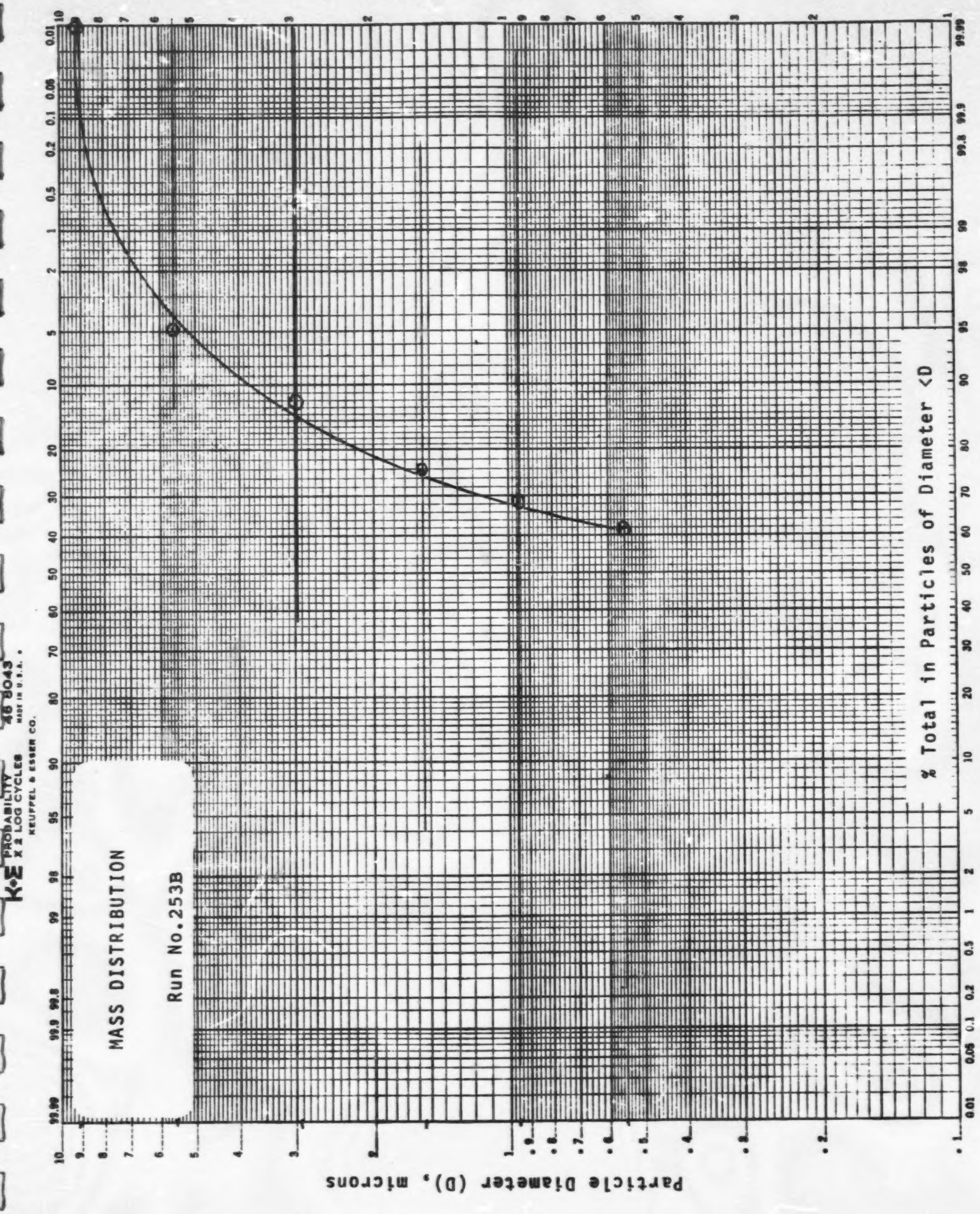
MASS DISTRIBUTION
Run No.253B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
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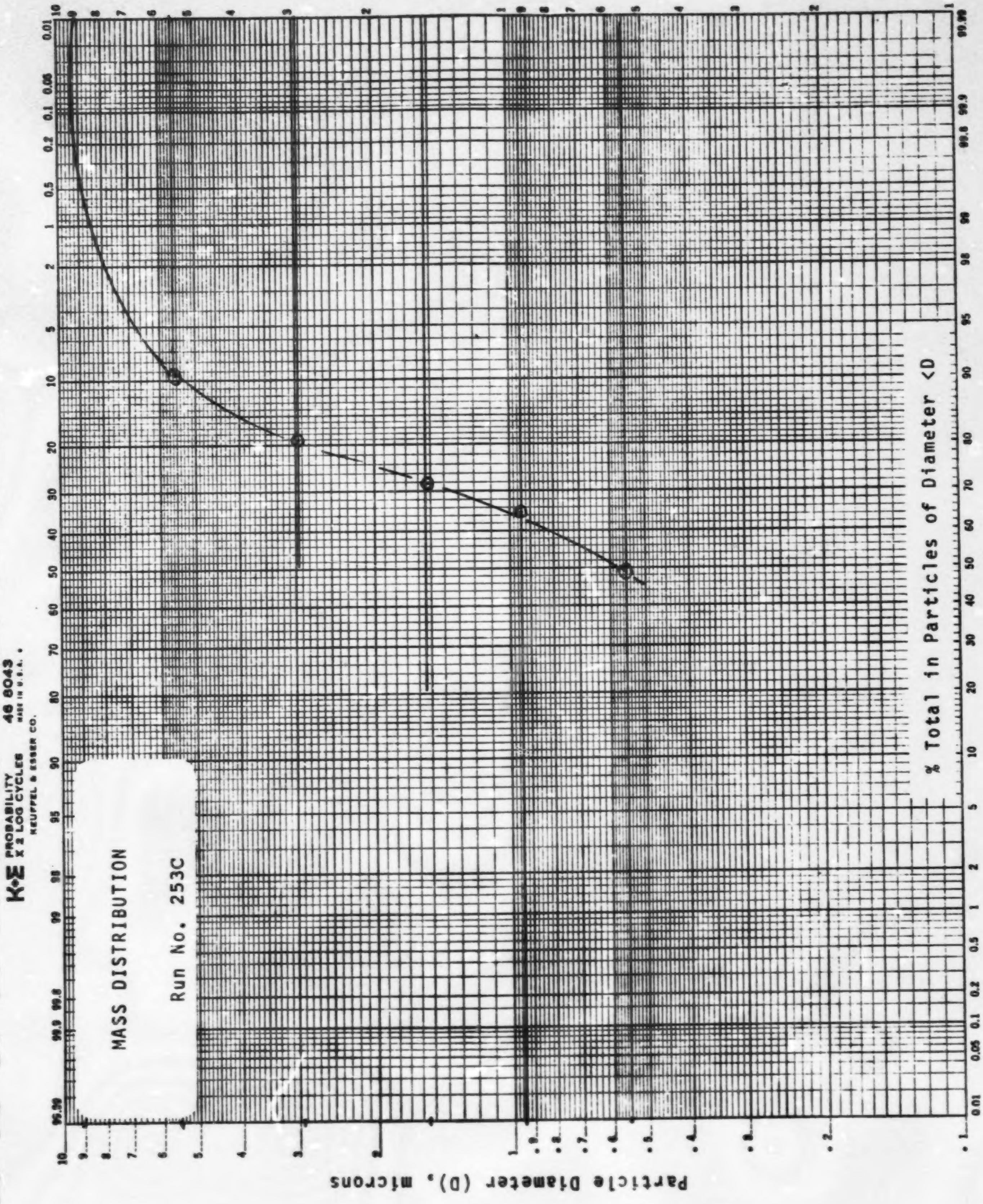
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
MADE IN U.S.A.


MASS DISTRIBUTION
Run No. 253C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
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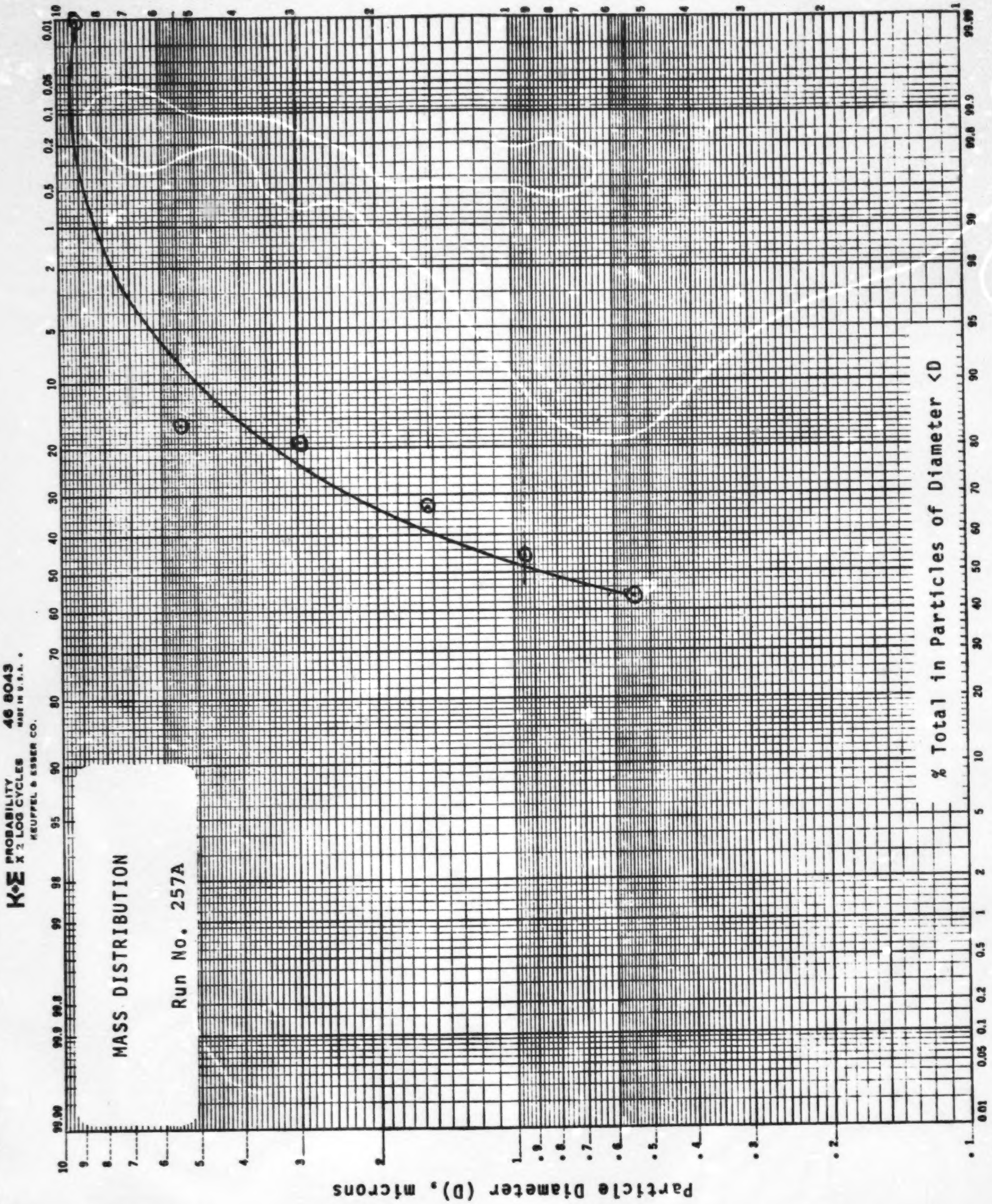
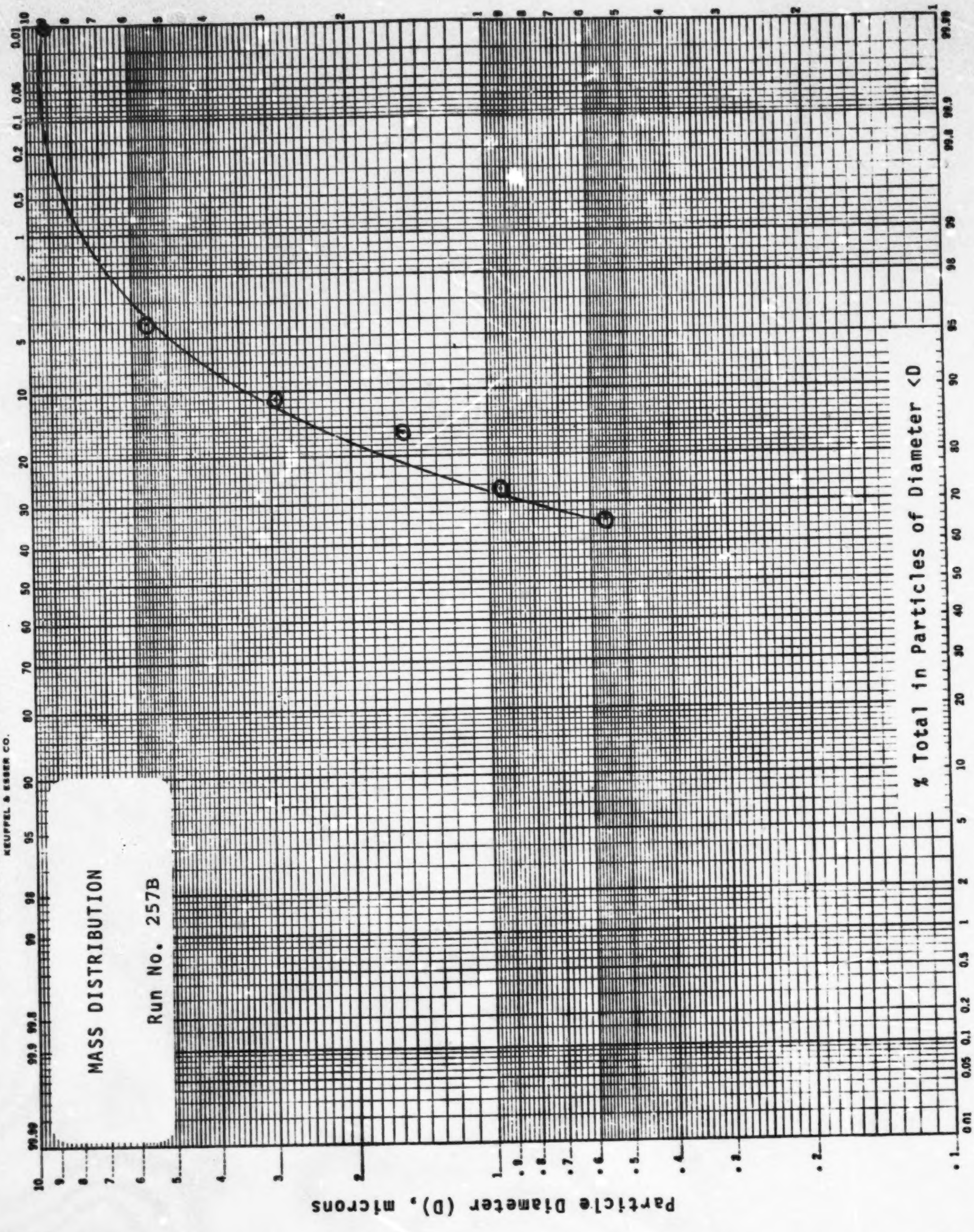
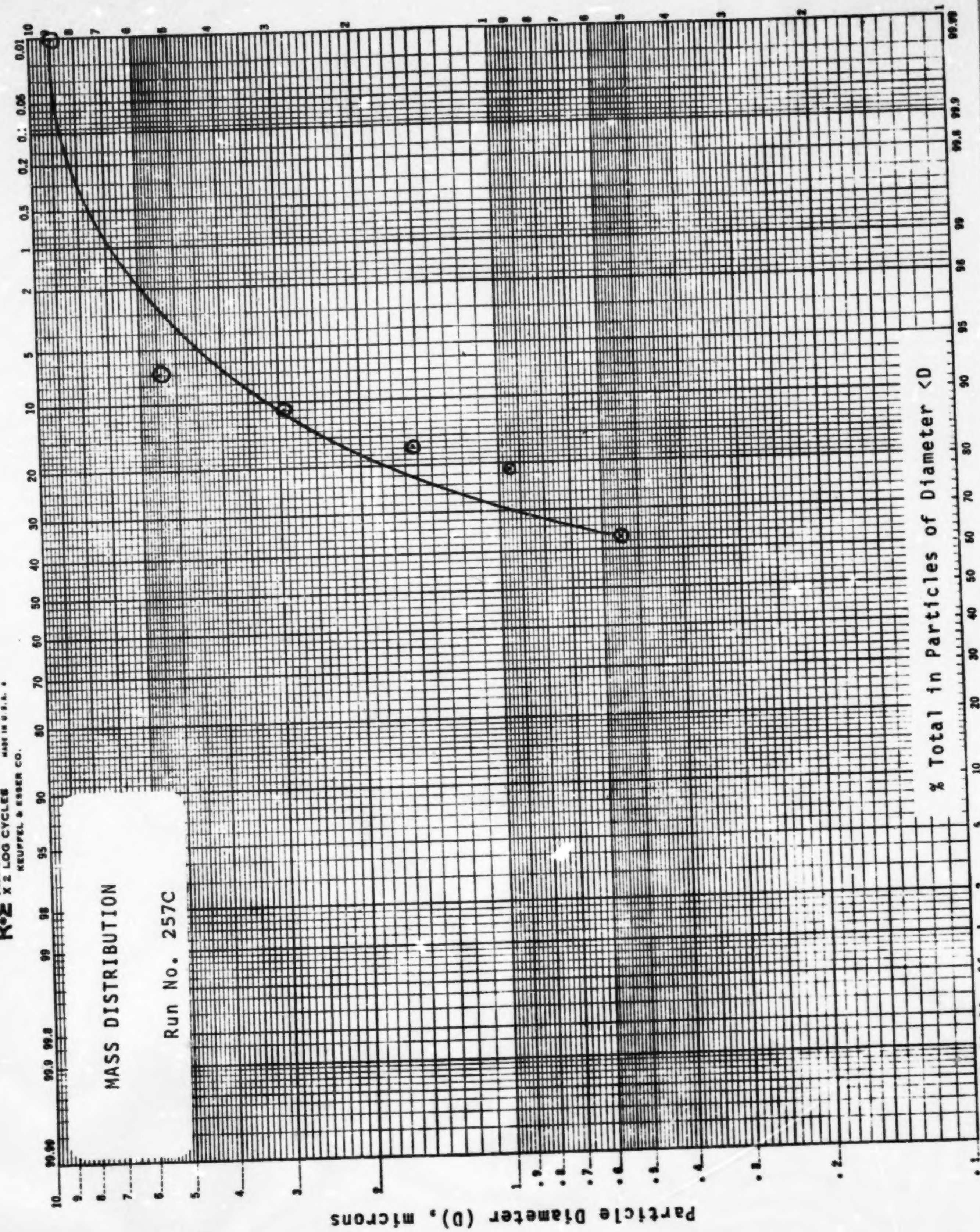
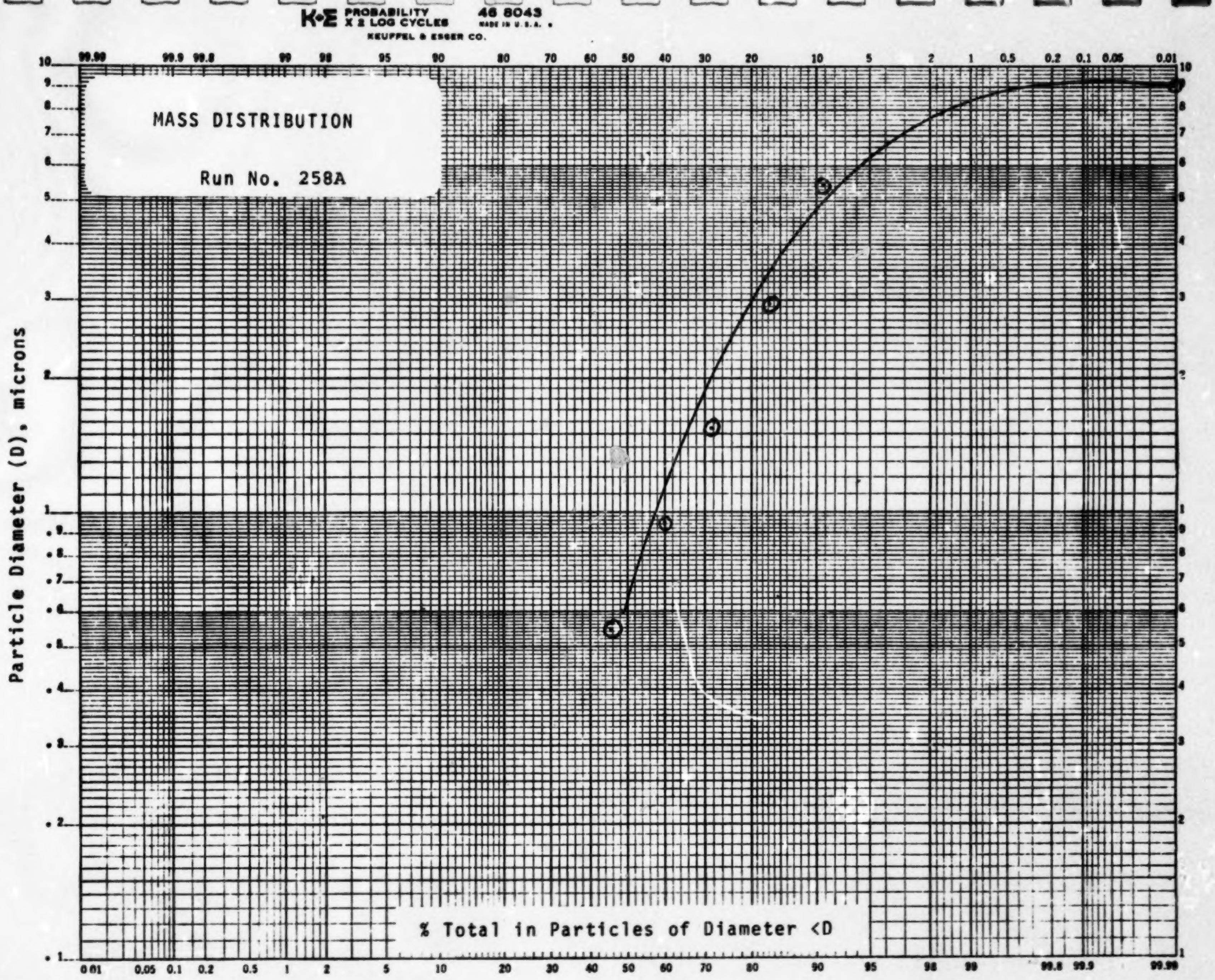
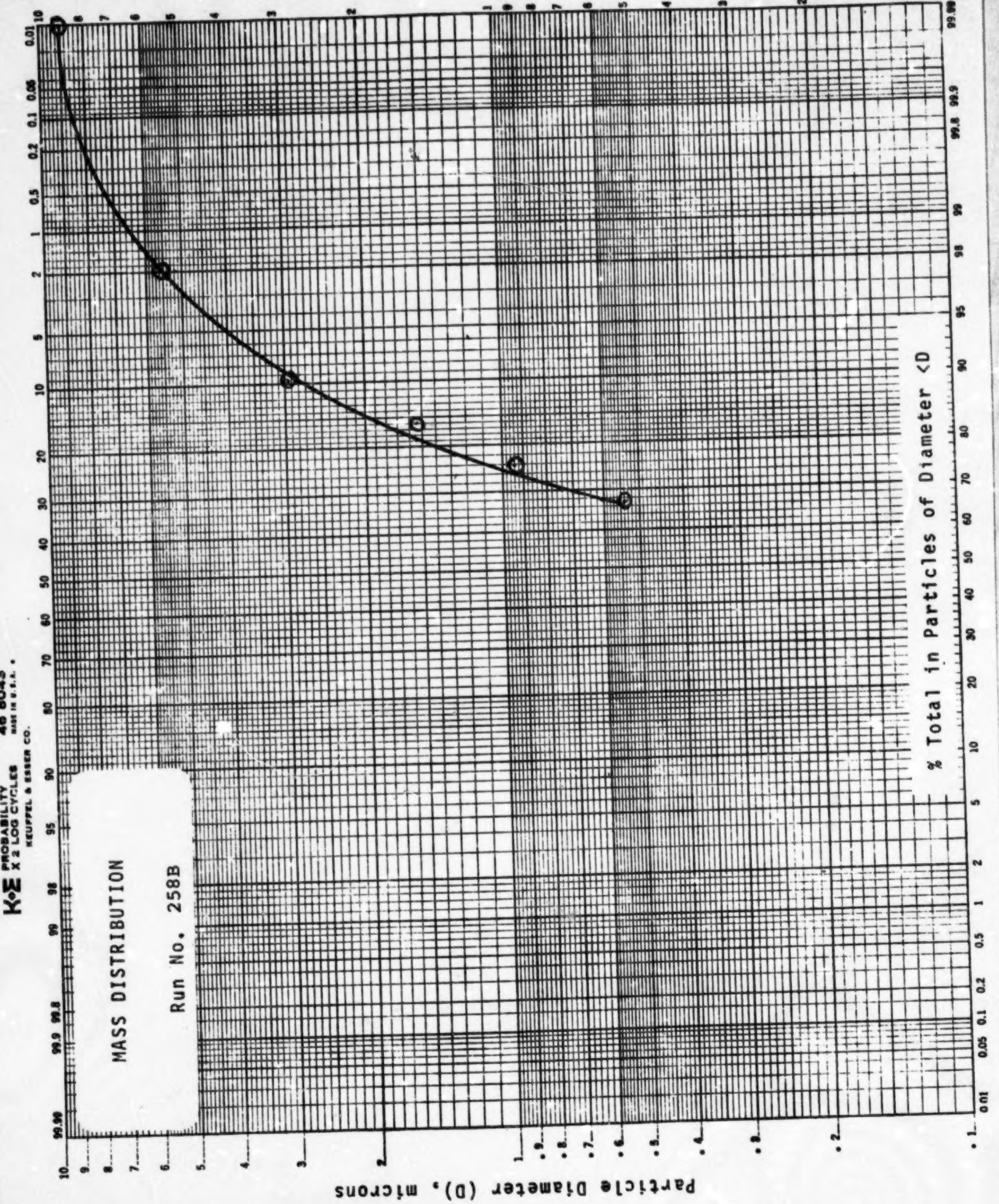
.2
.1

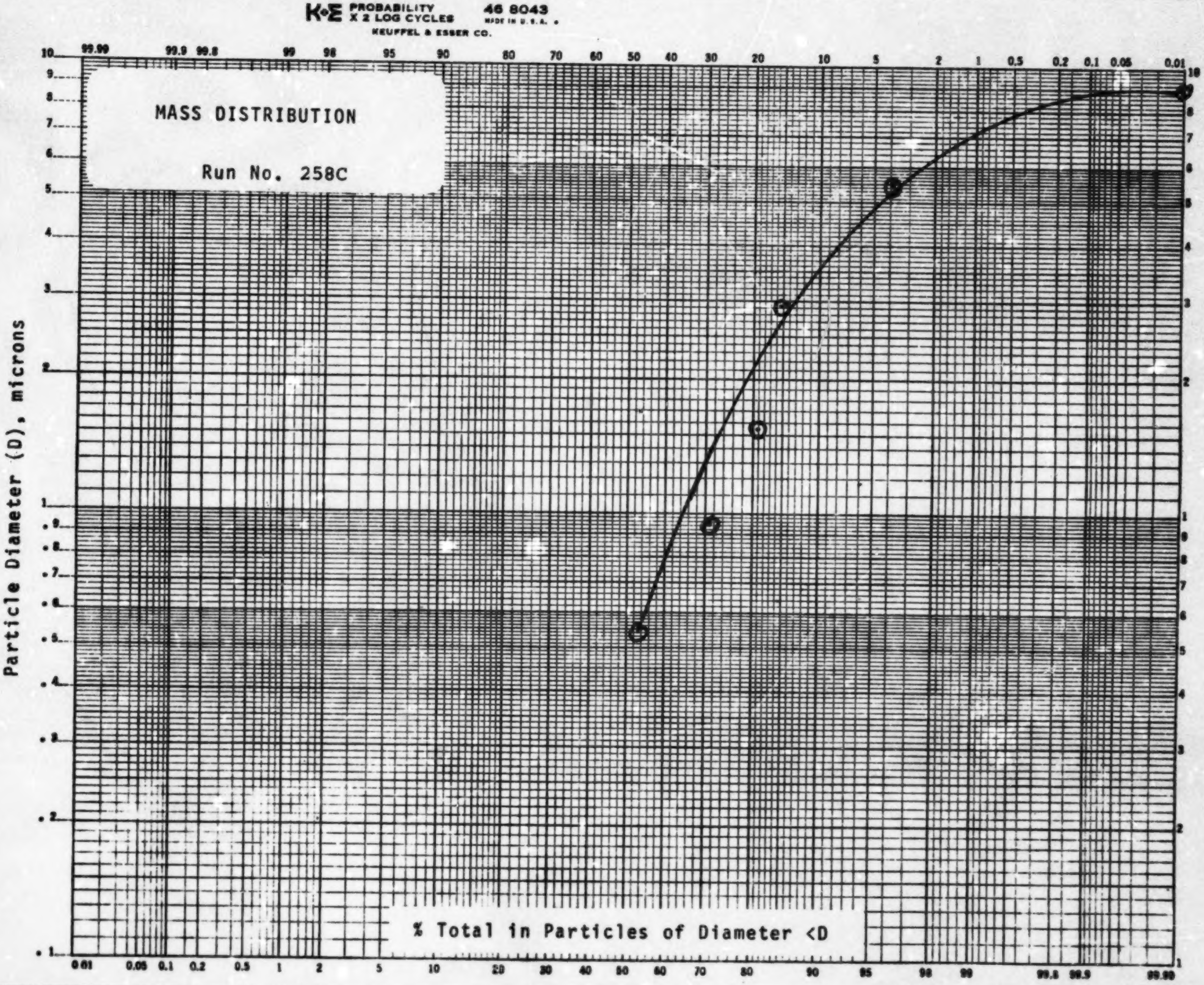

MASS DISTRIBUTION
Run No. 257A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 257B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1


MASS DISTRIBUTION
Run No. 257C
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K+E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

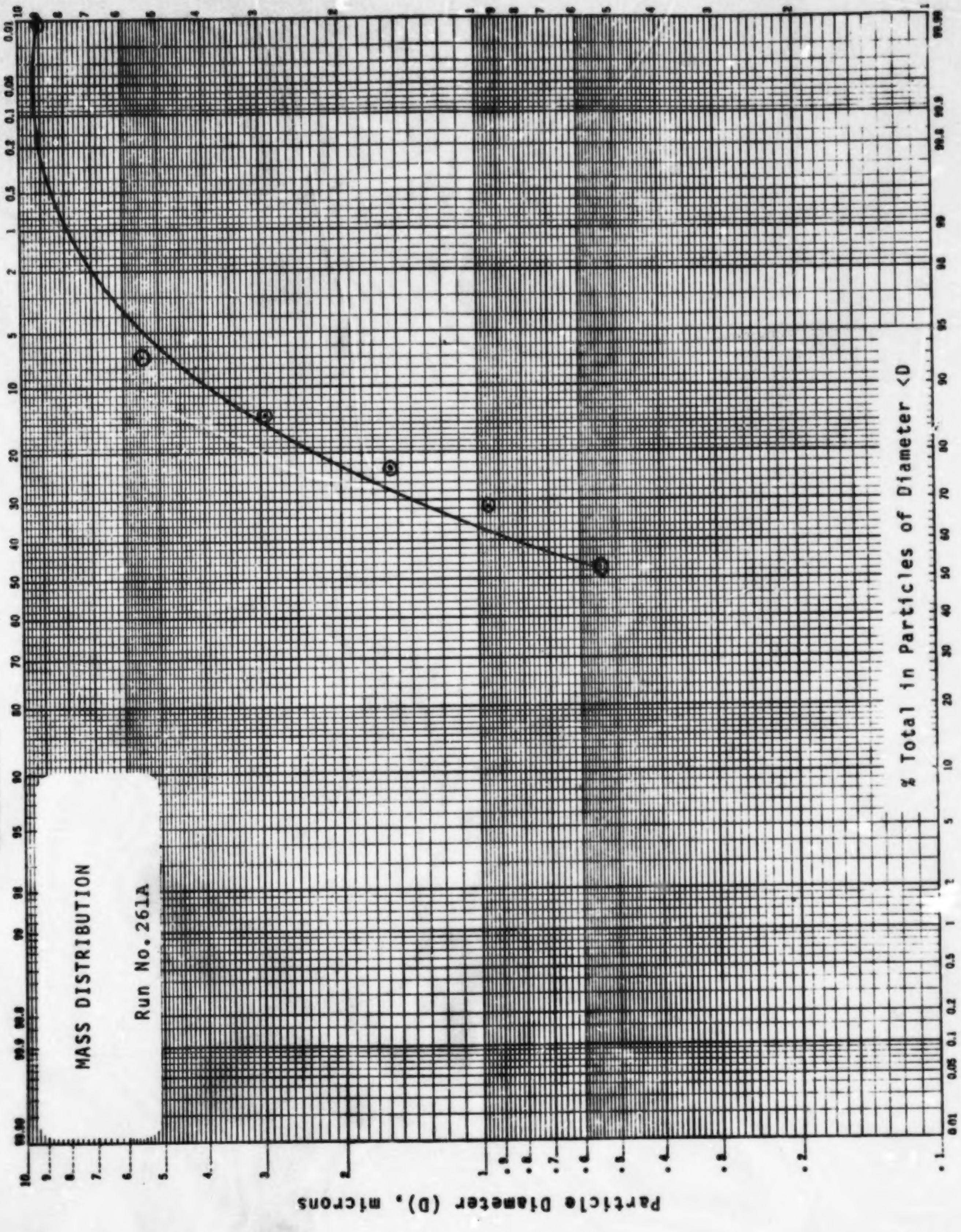

K+E PROBABILITY X 2 LOG CYCLES 46 8043
MADE IN U.S.A.
KEUFFEL & ESSER CO.
MASS DISTRIBUTION
Run No. 258A
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99


MASS DISTRIBUTION
Run No. 258B
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K&E PROBABILITY X 2 LOG CYCLES
46 8043
KEUFFEL & ESSER CO.
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1



MASS DISTRIBUTION

Run No. 258C


MASS DISTRIBUTION
Run No. 261A
% Total in Particles of Diameter <D
Particle Diameter (D), microns
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
9
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7
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5
4
3
2
1
.9
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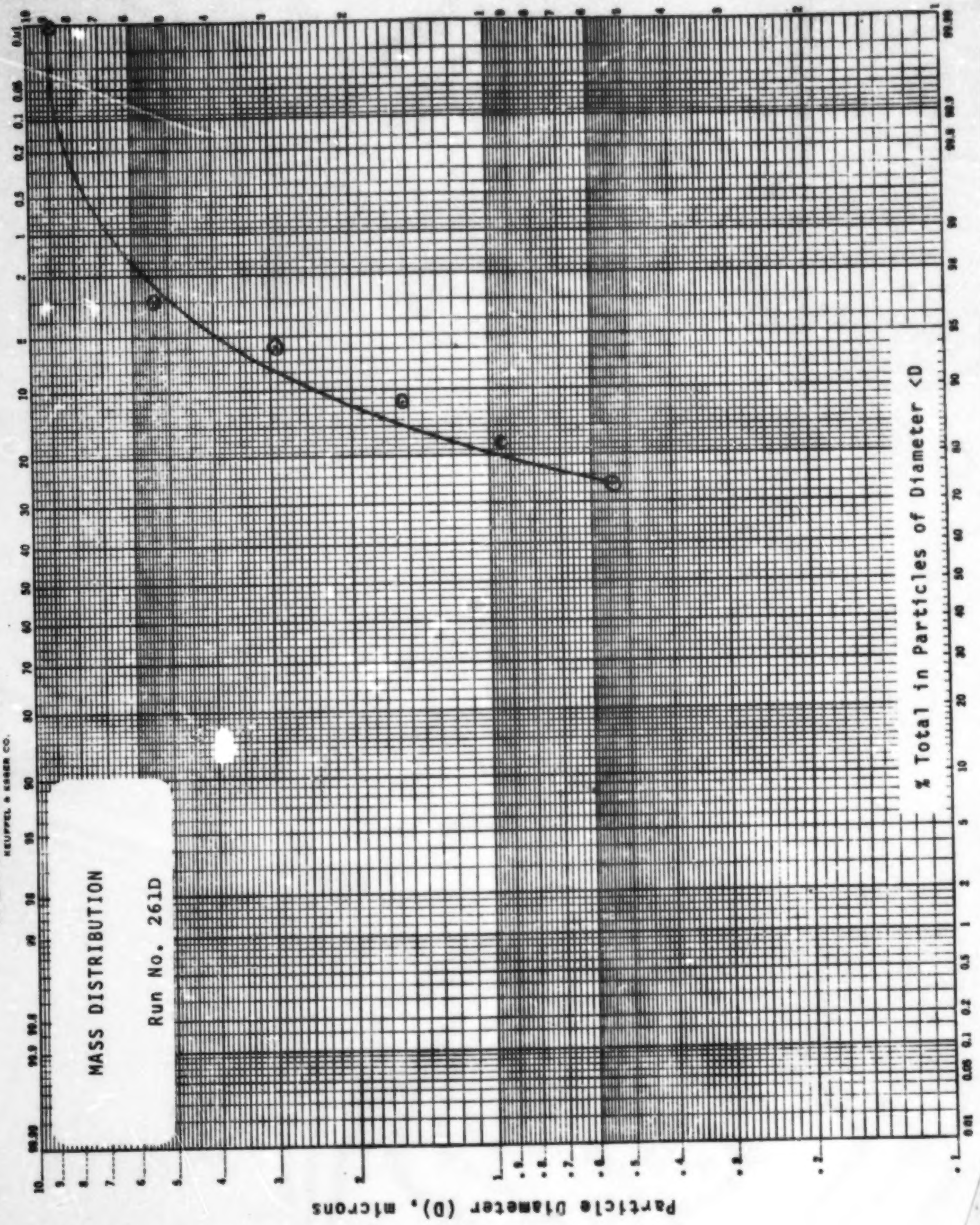
.4
.3
.2
.1
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.


MASS DISTRIBUTION
Run No. 261D
% Total in Particles of Diameter <D
Particle Diameter (D), microns
K•E PROBABILITY X 2 LOG CYCLES 46 8043 KEUFFEL & ESSER CO.
10
9
8
7
6
5
4
3
2
1
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.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99